(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 January 2017 (26.01.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/011873 A1

(51) International Patent Classification:
B01J 20/20 (2006.01) *B01D 53/02* (2006.01)
B01J 20/34 (2006.01) *B01D 53/32* (2006.01)

(21) International Application Number:
PCT/AU2016/050645

(22) International Filing Date:
20 July 2016 (20.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2015902863 20 July 2015 (20.07.2015) AU
2016900242 27 January 2016 (27.01.2016) AU

(71) Applicant: **NEWSOUTH INNOVATIONS PTY LIMITED** [AU/AU]; Rupert Myers Building, Gate 14, Barker Street, UNSW, Sydney, New South Wales 2052 (AU).

(72) Inventors: **SMITH, Sean C**; 8 Curtin Crescent, Maroubra, New South Wales 2035 (AU). **TAN, Xin**; 8/54 Middle Street, Kingsford, New South Wales 2032 (AU). **TAHINI, Hassan**; 4/18 Connemara Street, Bexley, New South Wales 2207 (AU).

(74) Agent: **GRIFFITH HACK**; Level 15, 300 Queen Street, Queensland, Queensland 4000 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHODS AND MATERIALS FOR CAPTURING AND STORING GAS

(57) Abstract: A system is described for storing gas in an adsorbent, the system comprising a gas permeable graphitic material. The graphitic material comprises carbon and at least one other element such as nitrogen and/or boron. The system also comprises an electrical source which allows the application of a first and second potential to the graphitic material. Upon application of the first potential, the gas is adsorbed to the graphitic material thereby producing a gas loaded material. Upon application of the second potential, at least some of the gas is desorbed from the gas loaded graphitic material.

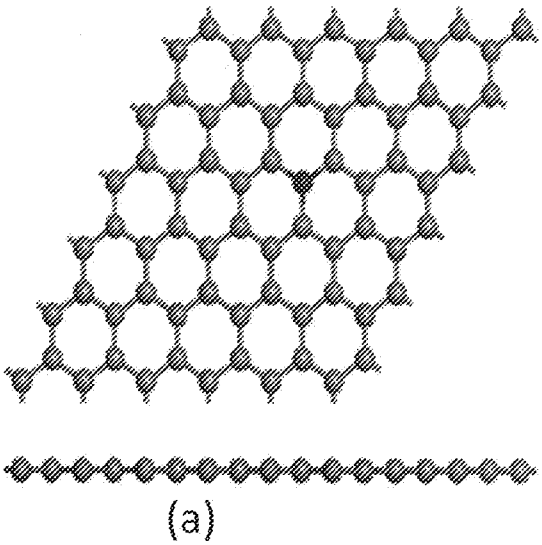

Figure 1

WO 2017/011873 A1

Published:

— *with international search report (Art. 21(3))*

Methods and materials for capturing and storing gas

This application claims priority from AU22015902863 and AU2016900242, both of which are hereby incorporated by reference in their entirety.

Technical Field

The present invention relates to materials that can be used for gas capture and storage. In one embodiment, the material is gas permeable graphitic material comprising at least two elements such as carbon and nitrogen; or carbon and boron. The material can be used for capturing gases such as carbon dioxide and/or hydrogen. In one embodiment, the material is a hydrogen storage material.

Background

Materials that can store gas have been used for a wide variety of applications, including energy storage and pollution control. Gases can be adsorbed onto a material for storage and the gas can subsequently be desorbed when the gas storage is no longer required. The materials that are used for such adsorption/desorption of gas typically have stringent requirements including that they preferably should be able to store a gas reversibly with large gravimetric and volumetric densities, and the adsorption/desorption process should not require significant energy inputs.

Light metal hydrides and chemical hydrides, for example, have been used as materials for gas adsorption/desorption. A gas that can be stored by these materials is hydrogen. In these systems, molecular H_2 typically needs to be split for adsorption. During subsequent desorption, the intrinsic free energy barrier for H recombination to form H_2 from the hydride needs to be overcome. When the intrinsic free energy H binding is high, the materials can be heated e.g. to greater than 200 ^{0}C to encourage desorption of the H_2 gas, but this presents a significant energy input. In some circumstances, the kinetics and thermodynamics of these adsorption/desorption processes is not favourable and can prevent the material from meeting requirements for commercial use.

Light-element-based materials, including carbon nanotubes or other carbon-based nanostructures, non-carbonaceous nanotubes, mesoporous silica, metal-organic frameworks, and covalent-organic frameworks can also be used as materials for gas adsorption/desorption. In these systems, molecular H_2 is usually weakly bound to the materials with adsorption energies in the meV range and hence the gas desorbs at very low temperatures. Such weak adsorption energetics requires the use of high pressures for sufficient storage to be achieved. Increasing the pressure can be a significant energy input,

as well as presenting safety hazards in the event of storage failure. Incorporating metals into the materials can improve the adsorption/desorption characteristics, but issues of clustering of the metal atoms and consequent degradation of the performance of the materials remains a challenge.

Accordingly, there exists a need for an improved method for capturing and/or storing gas, and an improved gas capture and/or storage material.

Summary

In a first aspect there is provided a method of adsorbing gas from a gas stream, the method comprising the steps of:

providing a gas permeable graphitic material comprising carbon and at least one other element;

allowing a gas to contact the graphitic material;

applying a first potential to the graphitic material to adsorb at least some of the gas thereby producing a gas loaded material; and

applying a second potential to the gas loaded material to desorb at least some of the gas.

The at least one other element can be nitrogen and the graphitic material can be carbon nitride or nitrogen-doped graphene. The at least one other element can be boron and the material can be boron-doped graphene.

In a second aspect there is provided an electrically conductive or semi-conductive adsorbent comprising a gas permeable graphitic material comprising carbon and at least one other element, when used under the influence of an electrical potential to adsorb a gas.

The at least one other element can be nitrogen. The graphitic material can therefore be a graphitic C-N material having a band gap less than about 2.5eV. The graphitic C-N material can have the formula CXNY, wherein X is ≤5 and Y is ≤5. Alternatively (or in addition), the graphitic material can be nitrogen-doped graphene. In some embodiments, the at least one other element is boron. The graphitic material can be boron-doped graphene. There can be less than about 25, 20, 15, 15, 5 wt% nitrogen or boron doping.

In a third aspect there is provided a system for storing gas in an adsorbent, the system comprising:

a gas permeable graphitic material as described herein,

an electrical source which allows the application of a first and second potential to the graphitic material,

wherein at the first potential the gas is adsorbed to the graphitic material thereby producing a gas loaded material, and wherein at the second potential at least some of the gas is desorbed from the gas loaded graphitic material.

The graphitic material comprises carbon and at least one other element. The at least one other element can be nitrogen and the graphitic material can be carbon nitride or nitrogen-doped graphene. When the other element is nitrogen the first potential is the injection of electrons in order to modulate the charge on the material; and the second potential is the removal of electrons in order to modulate the charge on the material. The at least one other element can be boron and the material can be boron-doped graphene. When the other element is boron, the first potential is the removal of electrons in order to modulate the charge on the material; and the second potential is the injection of electrons in order to modulate the charge on the material.

Description of figures

Embodiments are described, by way of example only, with reference to the accompanying non-limiting figures, in which:

Figure 1 shows embodiments of graphitic material comprising carbon and nitrogen.

Figure 1 (a) is a top (upper) and side (lower) view of a 6×6 single N-doped graphene supercell. The top and side views of the energy-optimized configurations of a single CO_2 molecule are shown absorbed on (b) neutral, (c) $2e^-$, (d) $4e^-$ (N site), (e) $4e^-$ (C site), and (f) $6e^-$ N-doped graphene. The distance between the C atom of CO_2 and the adsorption atom (C or N) and the adsorption energies of each configuration are listed.

Figure 1h shows a g-C_4N_3 supercell.

Figure 1j shows a g-C_3N_4 supercell.

Figure 1k shows a g-C_2N supercell.

Figure 1m shows a g-CN supercell.

Figure 2 shows the H–H bond length (Figure 2a), the distance between N atom and H_2 molecule (Figure 2b), the induced dipole moment of H_2 molecule (Figure 2c), and the adsorption energy of H_2 molecule (Figure 2d) as a function of the charge state of g-C_4N_3.

Figure 3a shows the relaxation of the physisorbed H_2 molecule to a chemisorbed structure when 3e- negative charge has been introduced into the g-C_4N_3 supercell.

Figure 3b shows the relaxation of the chemisorbed H_2 molecule (3e- charged g-C_4N_3 supercell) back to a physisorbed structure when the electrons are removed from the supercell.

Figure 4a shows the average adsorption energy of H_2 molecules on $3e^-$ negatively charged g-C_4N_3 at different hydrogen coverages - up to 12 molecules in the supercell.

Figure 4b shows the variation of the average adsorption energy of H_2 molecules at full coverage as the negative charge in the g-C_4N_3 supercell is increased from zero to 3e-.

Figure 5 shows the maximum number and the average adsorption energies of captured CO_2 molecules on negatively charged g-C_4N_3 with different negative charge densities.

Figure 6 shows the adsorption energies of CO_2, CH_4, H_2 and N_2 and H_2O on neutral, $1e^-$ and $2e^-$ negatively charged g-C_4N_3.

Figure 7 shows top and side views of the lowest-energy configurations of three CO_2 molecules absorbed onto the three C atoms adjacent to the N-dopant site in Figure 1(a) when 6 electrons are added. The distance between the C atom of CO_2 and the C atoms of graphitic N-doped graphene and the average adsorption energy are listed.

Figure 8 shows the adsorption energies of CO_2, CH_4, H_2, N_2 and H_2O on the neutral, 2e-, 4e- and 6e- N-doped graphene structure of Figure 1(a).

Figure 9(a) shows top views of the lowest-energy configurations and the calculated band structure of BC_{49}.

Figure 9(b) shows top views of the lowest-energy configurations and the calculated band structure of BC_7.

Figure 9(c) shows top views of the lowest-energy configurations and the calculated band structure of BC_5.

Figure 9(d) shows top views of the lowest-energy configurations and the calculated band structure of BC_3.

Figure 10(a) shows top and side views of the lowest-energy configurations of a single H_2 molecule absorbed on neutral BC_{49}.

Figure 10(b) shows top and side views of the lowest-energy configurations of a single H_2 molecule absorbed on 5e positively charged BC_{49}.

Figure 11(a) shows isosurface (0.06 e/au) of HOMO of neutral BC_{49}.

Figure 11(b) shows the differences in electron density distribution of 5e positively charged BC_{49} relative to neutral BC_{49} using frozen atomic geometry.

Figure 11(c) shows the differences in electron density distribution of a H_2 molecule adsorbed on 5e positively charged BC_{49} relative to neutral BC_{49} using frozen atomic geometry.

Figure 12(a) shows the adsorption energy of H_2 molecule for BC_{49}.

Figure 12(b) shows H-H bond length for BC_{49}.

Figure 12(c) shows induced dipole moment of H_2 molecule for BC_{49}.

Figure 12(d) shows H-B distance as a function of the positive charges of BC_{49}.

Figure 13(a) shows the energy change of the relaxation of a H_2 molecule on BC_{49} after five extra positive charges are introduced.

Figure 13(b) the reverse relaxation process of a H_2 molecule from BC_{49} after five extra positive charges are removed from the adsorbent.

Figure 14(a) shows top and side views of the lowest-energy configurations of 5e positively charged BC_{49} with two H_2 molecules electrocatalytically adsorption on each B atom

Figure 14(b) shows the average adsorption energies of positively charged BC_{49} with two adsorbed H_2 molecules as a function of the positive charges.

Figure 15(a) shows top and side views of the lowest-energy configurations of neutral BC_5.

Figure 15(b) shows top and side views of the lowest-energy configurations of 0.8e positively charged BC_5 with two H_2 molecules adsorption on each B atom.

Figure 15(c) shows average adsorption energies of positively charged BC_5 with two adsorbed H_2 molecules in each unit cell as a function of the positive charges.

Detailed Description

Materials

The graphitic material as described herein is carbonaceous and comprises carbon with at least one other element. The material can have its surface charge modulated upon the

application or removal of electrons as an applied potential. The material is able to reversibly adsorb a gas to its surface.

The at least one other element can be nitrogen. In one embodiment, the graphitic material comprises carbon and nitrogen. The material can be a carbon nitride. The material can be a nitrogen-doped graphene, which is essentially graphene with nitrogen doped into the graphene lattice. Experimental and theoretical studies have shown that you can only push N-doped graphene up to about 30% N, after which the continuous graphene mesh motif is not stable. In an embodiment there is less than about 25, 20, 15, 15 or 5 wt% nitrogen doping. Graphitic carbon nitride, on the other hand, whilst being a 2D material, is structurally different. Graphitic carbon nitride are based on hexagonal rings with alternating N-C-N-C and the structure has intrinsic pores in it rather than the continuous mesh that graphene and N-doped graphene have. The graphitic carbon and nitrogen containing material can be in the form of graphitic nanosheets, multi- and/or single-walled nanotubes (SWCNT), and/or fullerenes. Combinations of structures could be employed, for example, graphitic nanosheets used together with SWCNT.

The at least one other element can be boron. In one embodiment, the graphitic material comprises carbon and boron. The material can be a boron-doped graphene, which is essentially graphene with boron doped into the graphene lattice. In an embodiment there is less than about 25, 20, 15, 15 or 5 wt% nitrogen doping. The graphitic carbon and boron containing material can be in the form of graphitic nanosheets, multi- and/or single-walled nanotubes (SWCNT), and/or fullerenes. Combinations of structures could be employed, for example, graphitic nanosheets used together with SWCNT.

(i) Graphitic carbon nitride materials containing a large fraction of pyridinic N sites

With a focus on a material with a large number of pyridinic N moieties, graphitic carbon nitrides have attracted much attention over the past several years and would appear to be good candidates for electrolytic gas capture. Graphitic carbon nitrides can have a variety of molecular architectures. This is because nitrogen present in the carbon nitride structure can cause the material to adopt different chemical structures by creating different types of bonding, for example primary, secondary and tertiary forms of nitrogen bonding. The graphitic carbon nitride may include at least secondary and/or tertiary forms of nitrogen. In one embodiment, the carbonaceous graphitic material comprises nitrogen predominately in the secondary form.

The graphitic carbon nitride can be synthesised from precursor materials that are known to result in the desired chemical structure, which can be deduced by spectroscopy. The method

of the invention can include synthesising the graphitic material. The unit cell formula of graphitic carbon nitride can comprise carbon and nitrogen in a ratio of C_xN_y, where x = 1, 2, 3, 4 or 5 and y = 1, 2, 3, 4 or 5. The unit cell is the repeat unit that makes up the graphitic carbon nitride. In some embodiments, x = 4 and y = 3. In some embodiments, x = 3 and y = 4. Other variants, e.g., C_2N, CN, C_9N_7, are also possible where the ratio x/y lies in the ranges encompassed by these integers, i.e., between 0.2 and 5. The graphitic carbon nitride can be electrically conductive. For example, one conductive graphitic carbon nitride has the formula: C_4N_3 (x = 4 and y = 3) which comprises 3 of the carbon atoms and 3 of the nitrogen atoms arranged in a hexagonal ring, with the remaining carbon being bonded to one of the carbon atoms from the ring. This unit cell structure repeats to produce the graphitic type sheet structure.

The graphitic carbon nitride can be an electrical semi-conductor. For example, one semi-conducting graphitic carbon nitride has a unit cell formula of C_3N_4 (x = 3 and y = 4). Other graphitic carbon nitrides can be used, for example C_2N and CN. Additionally, a mixture two or more graphitic carbon nitrides can be used e.g. a mixture of C_4N_3 and C_3N_4 materials.

Dopants can be added to the graphitic carbon nitride lattice. The dopants can include boron, silicon, germanium. The presence of dopants can disrupt the unit cell formula. Introduction of dopants can be used to alter the electrical properties of the graphitic carbon nitride and may be used to adjust the band gap of the material. Metals such as lithium, beryllium, aluminium, palladium, platinum, ruthenium, (or any other metal known for use in conductors) can be included as a dopant. In some circumstances the dopant can also be a non-metal atom such as sulphur. A mixture of metal and non-metal dopants can be used. The dopant can be introduced during synthesis of the graphitic carbon nitride. The total amount of doping can be less than about 1, 5, 10 or 20 % by weight.

(ii) Nitrogen-doped graphene

Substitutional N-doped graphene is the dominant energetically favoured defect site occurring when N is doped into graphene. It has been demonstrated both experimentally and theoretically that substitutional N doping can be pushed as high as 30 % nitrogen content. The N-doped graphene material is conducting (metallic), which is a very important feature to effect the addition of charge to the material for the electrocatalytic gas binding. In contrast with the conducting g-C_4N_3 (which has only been inferred in one experimental paper to date), synthetic procedures to make such N-doped graphene are now well established.

(iii) Boron-doped graphene

Hexagonal-like B-doped graphenes with B content less than 50 % have been synthesized. The structure determines whether the B-doped graphene is a conductor (metallic) or a semiconductor. Typically, less than 30 wt% of boron doping results in a conductor. For example, metallic B-doped graphene has a structure ranging from BC_{49}-BC_5, while semiconductor graphene has a structure of BC_3. B-doped graphene with B content ranging from 0 to 20 atom %, preferably 0 to 16.7 atom %, has good electrical conductivity and high electron mobility.

Gas adsorption and desorption

The gas permeable carbon and other element containing material is an adsorbent for gas. This means that gas molecules are able to interact with at least some of the atoms in the graphitic lattice. The interaction of the gas with the graphitic material can be by a covalent, ionic and/or Van der Waals type of bonding. The gas adsorption and desorption is performed by charge modulation of the underlying graphitic material.

The permeability to gas can be a result of the porosity of the gas permeable material. Nanosheets such as graphitic carbon nitride, or N-or B-doped graphene, have a natural porosity along a 2D plane, while nanotubes have a natural porosity along a longitudinal axis of the tube. Accordingly, mixtures of different forms of graphitic material can be used to control the porosity of the gas permeable material, and this may alter the adsorption and/or desorption characteristics. Gas can be delivered to the material at a flow rate that allows at least some of the gas to permeate the material and be adsorbed thereon.

The gas that is adsorbed can be a pure gas, a substantially pure gas, or a mixture of gases. In an embodiment, the gas is selected from hydrogen, carbon dioxide, nitrogen, methane and mixtures thereof. Other commercially relevant gases, such as argon, helium and oxygen, may also be adsorbed.

The gas adsorption can be for separation of a gas from a stream comprising a mixture of gases. In the case of substantially pure or a mixtures of gases, the carbonaceous absorbent material may selectively adsorb one gas. For example, in a gas stream comprising nitrogen and carbon dioxide, the material may selectively adsorb carbon dioxide. This selective adsorption property may enable the material and method to be used as or during a purifying step in gas production and/or separation, for example removal of carbon dioxide from natural gas in the liquefied natural gas industry. This selective adsorption property may also allow for the selective adsorption of gases that are produced as a by-product from industrial application, for example carbon dioxide produced from coal fire power stations. Being able to selectively adsorb one gas means that the graphitic material can also be used as an

indicator and/or detector to detect the presence of a gas in a gas stream. It may be advantageous to detect trace amounts of a particular gas in a gas stream, for example detecting trace amounts of carbon dioxide in a nitrogen stream. Upon adsorption of a target gas the detector could indicate to the user that a particular gas has been adsorbed. This may be by detecting a change in the weight of the material. The change in weight might be known to only be possible upon the adsorption of the particular target gas.

The amount of gas that is adsorbed onto the graphitic material can be related to (and thus controlled) by the electrical and/or chemical characteristics of the graphitic material. In one embodiment, the graphitic material adsorbs at least about 3, 5, 6, 7, 8, 10, 20, 30 or 40 wt.% gas. The higher the molecular weight of the gas, the more wt% that the material may absorb. In an embodiment, a graphitic carbon nitride adsorbs about 6 to 7wt.% hydrogen. In an embodiment, an N-doped graphene material may adsorbs about 40 wt.% carbon dioxide. In an embodiment, B-doped graphene adsorbs about 5 to 6 wt% such as 5.3 wt.% hydrogen. For some gases, such as carbon dioxide, it may be advantageous to adsorb as much gas as the graphitic material will allow.

(i) Hydrogen gas

The graphitic carbon nitrides seem to be the most useful for adsorbing both H_2 and CO_2. The B-doped graphene can be useful for adsorbing hydrogen. The loading of e.g. the graphitic carbon nitride or the B-doped graphene with at least 5 wt.% gas can mean that the graphitic materials are suitable for application as a hydrogen storage material. Hydrogen storage materials find use for example in hydrogen powered cars. In terms of gas storage, the kinetics and thermodynamics of desorption is a critical step in being able to deliver gas on demand without significant delay.

Once loaded with gas, the gas loaded material can be stored, handled, transported. The gas-loaded material should remain in the loaded state, for as long as the first potential is applied to it. The material can be stable for months, weeks or days.

(ii) Carbon dioxide gas

At the current rate of emissions of greenhouse gases, for which carbon dioxide (CO_2) is the main component, global warming and climate change will continue to rise. One crucial issue in efficiently separating, capturing, storing and/or converting CO_2 is the development of a practical sorbent material. Liquid-amine, which is the most common adsorbent in current industrial processes for CO_2 capture, suffers from relatively low efficiency, equipment corrosion, solvent loss, and toxicity. Alternatively, various solid materials have been

proposed as attractive adsorbents for CO_2 capture, including metal-organic frameworks (MOFs), aluminum nitride (AlN), carbon, hexagonal boron nitride (h-BN), and silicon carbide (SiC) nanostructures. However, the difficulty of regeneration due to the large adsorption energy, which generally demands high temperatures to release captured CO_2, significantly hinders the practical application of such materials. Typically, a temperature / pressure swing adsorption approach is used to selectively capture CO_2 out of a mixed gas stream at ambient temperature and pressure; subsequently releasing it in purer form at low pressure and/or raised temperature. The latter stage is costly due to the energy input for heating.

The N-doped graphene materials seem to be the most useful for absorbing CO_2.

Electrical activity

In order to encourage gas adsorption, electrons can be injected or removed from the graphitic material depending upon the chemistry of the material. For example, electrons can be injected into the graphitic C-N material (carbon nitrides or N-doped graphenes) to encourage gas adsorption. For example, electrons can be removed from B-doped graphene to encourages gas adsorption to a positively charged surface. The injection and removal of electrons can be by the application of an electrical current or voltage. Calculations show that the injection of electrons causes the surface of the graphitic C-N material to be more attractive to the gas while removal of electrons causes the surface of the B-doped graphene to be more attractive to the gas, which then binds to the electrically charged surface. The charge on the surface can therefore be modulated by the applied potentials.

If the graphitic material has an inherent band gap then this will impact how much potential needs to be applied to encourage gas adsorption. Lower band gap values usually means a relatively low electrical potential is required for adsorption of a gas compared to a higher band gap material. Accordingly, graphitic materials (semi-conductors e.g. carbon nitride) with band gaps less than about 5, 4, 3, 2.5 or 2 eV can be most suitable for gas adsorption/desorption. Larger band gaps materials can be used in conjunction with a conducting substrate to facilitate charging.

A first potential can be applied to adsorb at least some gas onto the graphitic material. A second potential can be applied to desorb at least some of the adsorbed gas from the graphitic material. The second potential can be applied subsequent to the first potential. A first and second potential can be applied cyclically.

To apply the first and second potentials, the graphitic material can be in contact with an electrical source. The electrical source can be an electrode in direct contact with an

inherently electrically conductive graphitic material. In one embodiment, the electrode can be a layer associated with the gas permeable material. In this case, the gas permeable material can be applied as a thin film onto the surface of an electrically conductive substrate. The layer of electrically conductive material can comprise a metal oxide, or a noble metal. The layer can be e.g. ITO, or gold, or it could comprise an electrically conductive carbon material.

The gas permeable carbon and nitrogen; or carbon and boron containing material can increase in electrical conductivity by mixing it with a conductive material. The conductive material can be carbon black or graphene. The mixture can have the electrical potential applied by a point contact, and/or the mixture can be applied onto a surface of a conductive substrate in contact with the electrodes. A conductive adhesive may be included in the conductive mixture to adhere the conductive mixture to the substrate.

Gas adsorption can occur upon exposure of the material to a first potential. The first potential can be less than about 100, 80, 90, 70, 60, 50, 40, 30, 20 or 10 volts. In some embodiments, the first potential is less than about 10 volts. In one embodiment, the applied voltage is at most about 8, 6, 4, 2 volts from a standard hydrogen electrode. In another embodiment, about 1 volt is applied to cause the adsorption of gas. Optionally, the first potential is varied (this can be controlled) to adjust the amount of gas adsorbed. Prior experiments can be undertaken to determine how much gas will be adsorbed at various applied potentials. The advantage of relatively low voltage values is that they can help to reduce energy input and may make use of the carbonaceous material safer from an electrical hazard view point, for example minimizing electrical discharge which can be especially important for hydrogen storage or the storage of other combustible gases.

In order to encourage gas desorption, injected electrons can be removed from the graphitic material, In order to encourage gas desorption, electrons can be injected into the B-doped graphene. Gas desorption can occur upon exposure to the second potential. The second potential is determined relative to the first potential. The potential values required to adsorb and desorb gas can be related to the band gap of the graphitic material.

The second potential can be less than the first potential. In one embodiment, the second potential is 80, 70, 60 or 50% less than the first potential. Optionally, the potential is varied (this can be controlled) to adjust the amount of gas desorbed. In one embodiment, the second potential is 0 volts (which means that any electrical potential is effectively removed from the system). The spontaneous discharge of excess electrons may need assistance. At 0 volts, substantially all of the adsorbed gas in the gas loaded graphitic material may be desorbed.

The second potential can be greater than the first potential. In one embodiment, the second potential is 80, 70, 60 or 50% higher than the first potential. Optionally, the potential is varied (this can be controlled) to adjust the amount of gas desorbed

A vacuum may be applied before or after the second potential is reached to aid desorption of gas. Likewise, after a gas has been adsorbed, the volume of air surrounding the graphitic material may be flushed prior to desorption. Desorption may be performed in steps to prevent a sudden increase in pressure. For example, the first and the second potential may alternatively be switched where the second potential is applied for a longer period of time than the first potential. In this way, release of the gas can be performed by repeated adsorption/desorption steps that result in a net desorption. A gradient potential change between the second and first potential may be used to achieve a steady state release of gas. However, it may be desirable that the gas is desorbed in one sudden step. An algorithm can be used to control the switching between applied potentials.

Multiple gas effects

Due to the characteristics of the graphitic material, adsorption and desorption of gas can occur spontaneously without any energy barriers once extra electrons are injected or removed by switching between the first or second electrical potentials.

The graphitic C-N material may adsorb a particular gas from a gas stream, when a certain threshold of electrons are injected . A second different gas may be adsorbed when more electrons are injected. In such cases, a first potential can cause the adsorption of a first gas; a further applied potential that is greater than the first potential can adsorb a second gas from a gas stream. To enable a multi gas adsorption, the relative potentials required for adsorption and desorption of each gas may be such that transitioning between the different potentials would adsorb/desorb only one gas. However, it may be advantageous to adsorb and/or desorb two or more gasses at the same time. An algorithm can be used to control the switching between the different potentials for multiple gas adsorption/desorption.

The graphitic C-B material may adsorb a particular gas from a gas stream, when a certain threshold of electrons are removed . A second different gas may be adsorbed when more electrons are removed. In such cases, a first potential can cause the desorption of a first gas; a further applied potential that is less than the first potential can desorb a second gas from a gas stream. To enable a multi gas adsorption, the relative potentials required for adsorption and desorption of each gas may be such that transitioning between the different potentials would adsorb/desorb only one gas. However, it may be advantageous to adsorb

and/or desorb two or more gasses at the same time. An algorithm can be used to control the switching between the different potentials for multiple gas adsorption/desorption.

A combination of carbonaceous materials, e.g. a combination of N-doped graphene and B-doped graphene may be used to adsorb two or more different gases. There may be one or more electrical systems to control the potentials of the different types of carbonaceous graphitic materials.

When multiple gases are adsorbed onto a carbonaceous graphitic material(s), the amount of first gas adsorbed is generally less than the total adsorption capacity of the carbonaceous material. If the carbonaceous material is overloaded with the first gas, it may not be able to adsorb the second gas. If two different carbonaceous materials are used where each carbonaceous material selectively binds a different gas e.g. N-doped graphene for CO_2 adsorption and B-doped graphene for H_2 adsorption, then each carbonaceous material may be overloaded with adsorbed gas without affecting the loading capacity of the other carbonaceous material.

Temperature effects

Typically, the temperature required for gas desorption is greater than the temperature required for gas adsorption. An advantage of the materials described here is that desorption may not require elevated temperatures and may instead rely only on the removal of the first potential to provide the second potential. The second potential can be 0 volts. In these circumstances, desorption may be performed at temperatures approximate to that of the adsorption process. Accordingly, desorption may be performed at a temperature less than about 100 ^{0}C, 75 ^{0}C or 50 ^{0}C. In an embodiment, desorption is performed at approximately room temperature.

The temperatures used are related to the way in which the graphitic material binds the gas. The graphitic materials can adsorb gas in its molecular form. This is in contrast with, for example, metal hydrides which typically require the use of catalysts to split gases such as hydrogen to adsorb the gas in elemental form. Adsorbing gas in its molecular form (e.g. H_2) may mean the use of graphitic materials can significantly reduce the energy barrier required for adsorption and desorption because there is no need to break and reform bonds i.e. energy inputs such as temperature can be significantly reduced. Meanwhile, the electrical response which mediates the strength of binding means that high pressures are not necessarily required to adsorb gas onto the graphitic carbon nitride.

The system

The graphitic materials can be used in a system which comprises an electrical source to apply the first and second potentials. The system may comprise sensors to determine the pressure of the gas before, during and/or after adsorption and/or desorption of the gas. The sensors may communicate with a computer. The computer may instruct the electrical source. When the pressure falls below a predetermined value, the computer may instruct the electrical source to apply the second potential to desorb gas. Likewise, when the pressure increases above a predetermined vale, the computer may instruct the electrical source to apply the first potential to adsorb more gas. More than one computer can be used to instruct the electrical source(s).

The system may comprise a temperature regulator. The temperature regulator may heat and cool the system, and may also be instructed by a computer. This computer may be the same or different to the computer that instructs the electrical source. Where different computers are used to instruct the temperature regulator and the electrical source, the two computers can communicate with one another.

In the system, the material can be contained in a voluminous body. The desorbed gas may be stored in this voluminous body and/or stored in an intermediate chamber in communication with the voluminous body.

The system may comprise pressure relief valves in communication with the voluminous body. Pressure relief valves may operate when the system fails and there is sudden desorbing of gas. These valves may operate with and/or without the input from a computer. The values may communicate with the pressure sensors.

Synthesis of the carbonaceous material

The graphitic carbon nitride can be synthesized by cross-linking nitride-containing anions in an ionic liquid or other suitable precursor materials such as ammonia. In situations where the graphitic C-N material is provided on a conductive substrate, the graphitic C-N material can be synthesized directly onto an electrically conductive substrate.

B-doped graphene can be prepared using solid phase, liquid phase, chemical vapour deposition, or post-functionalization of graphene. As an example of solid state synthesis, graphite powder and a boron precursor, such as mainly H_3BO_3, B_2O_3 or B_4C, are combined then boron doped graphite can be mechanically exfoliated in order to obtain single sheets of B-doped graphene. Alternatively, B-doped graphene can be synthesized directly on to an electrical conductive substrate.

Examples

Calculations

Carbon nitrides

DFT calculations employed the linear combination of atomic orbital and spin-unrestricted method implemented in Dmol^3 package [*Zhao et al., J. Chem. Theory Comput. 2009, 5, 1099–1105*]. The generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) functional form [*Zhang et al., RSC Adv. 2014, 4, 48994– 48999*] together with an all-electron double numerical basis set with polarization function (DNP) was adopted. Since the standard PBE functional is incapable of giving an accurate description of weak (van der Waals, vdW) interactions, a DFT+D (D stands for dispersion) approach was adopted in the computations with the Ortmann−Bechstedt−Schmidt (OBS) vdW correction [*Sun et al., J. Am. Chem. Soc. 2013, 135, 8246–8253*]. The real-space global cutoff radius was set to be 4.1 Å.

2×2 and 2×1 supercells for g-C_4N_3 were employed with periodic boundary conditions in the x-y plane. The vacuum space was set to larger than 20 Å in the z direction to avoid interactions between periodic images. In geometry optimizations, all the atomic coordinates were fully relaxed up to the residual atomic forces smaller than 0.001 Ha/Å, and the total energy was converged to 10^{-5} Ha. The Brillouin zone integration was performed on a (6×6×1) and (4×8×1) Monkhorst-Pack k-point mesh [*Tan et al., ChemSusChem 2015 (in press)*] for g-C_4N_3 and g-C_3N_4, respectively.

The adsorption energy $Eads$ of H_2 molecules on adsorbent was defined as

$$Eads=(Eadsorbent+nEH_2-Eadsorbent-nH_2)/n,$$

where $Eadsorbent$ is the total energy of isolated g-C_4N_3 or g-C_3N_4; EH_2 is the total energy of an isolated H_2 molecule; $Eadsorbent-nH2$ is the total energy of adsorbent with adsorbed H_2 molecules; and n is the number of H_2 molecules adsorbed on adsorbent. According to this definition, a more positive adsorption energy indicates a stronger binding of H_2 molecule to adsorbent. The electron distribution and transfer mechanism are determined using the Mulliken method [e.g. *Du et al., Phys. Rev. Lett. 2012, 108, 197207*].

Boron-doped graphene

DFT calculations employed the linear combination of atomic orbital and spin-unrestricted method implemented in Dmol3 package [*Delley, J. Chem. Phys. 2000, 113, 7756–7764*]. The generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) functional

form [*Perdew et al., Phys. Rev. B 1992, 45, 13244–13249*] together with an all-electron double numerical basis set with polarization function (DNP) were adopted. Since the standard PBE functional is incapable of giving an accurate description of weak interactions, we adopted a DFT+D (D stands for dispersion) approach with the Grimme's vdW correction in our computations [*Grimme et al.. J. Comput. Chem. 2006, 27, 1787–1799*]. The real-space global cutoff radius was set to be 4.3 Å.

To simulate B-doped graphene nanosheets with increase of B content, BC49, BC7, BC5 and BC3 were considered. 1×1 supercells were used to study the interaction between H_2 molecules and B-doped graphene with periodic boundary conditions in the x-y plane. The vacuum space was set to larger than 20 Å in the z direction to avoid interactions between periodic images. In geometry optimizations, all the atomic coordinates were fully relaxed up to the residual atomic forces smaller than 0.001 Ha/Å, and the total energy was converged to 10-5 Ha. The Brillouin zone integration was performed on a (5×5×1), (12×12×1), (13×13×1) and (12×12×1) Monkhorst–Pack k-point mesh [*Monkhorst et al. Phys. Rev. B 1976, 13, 5188–5192*] for BC49, BC7, BC5 and BC3, respectively.

The adsorption energy $Eads$ of H_2 molecules on adsorbent was defined as

$$Eads=(Eadsorbent+nEH_2-Eadsorbent-nH_2)/n,$$

where $Eadsorbent$ is the total energy of isolated g-C_4N_3 or g-C_3N_4; EH_2 is the total energy of an isolated H_2 molecule; $Eadsorbent-nH2$ is the total energy of adsorbent with adsorbed H_2 molecules; and n is the number of H_2 molecules adsorbed on adsorbent. According to this definition, a more positive adsorption energy indicates a stronger binding of the H_2 molecules to adsorbent. The electron distribution and transfer mechanism are determined using the Mulliken method [*Mulliken, J. Chem. Phys. 1955, 23, 1833–1840*].

Material design

Nitrogen doped carbon nanotubes or graphenes with pyridinic-nitrogen defects have the advantage of relatively good electrical conductivity, so that charge can be readily added or removed by manipulating voltage. However, pyridinic nitrogen is a minority defect structure in comparison with substitutional Nitrogen doping; hence the question arises: how to dope a sufficient density of pyridinic Nitrogen defect sites into carbon nanotubes or graphene so as to enable efficient gas capture. To deal with these issues, two design strategies present themselves:

(i) Seek a material with large amounts of pyridinic nitrogen – ideally conductive; or

(ii) Focus on the majority N-dopant structure in graphitic carbon: substitutional N-doping.

The material design typically focuses on an approach of electrocatalytic gas capture that can offer advantages of controllable kinetics and reversibility. For example, while CO_2 molecules are predicted to be weakly adsorbed (i.e., physisorbed) on neutral substitutional N-dopant or pyridinic N sites in graphenes; when negative charge is simulated in a supercell, density functional theory (DFT) calculations reveal that CO_2 adsorption can be dramatically enhanced via a charge-induced chemisorption interaction. CO_2 is not transformed chemically in this process (although this eventuality should not be excluded and could be highly desirable). However, the phrase *electrocatalytic* gas capture is likely most appropriate, since the presence of charge is both quantitatively and qualitatively changing the chemical interactions (i.e., the potential energy surface) in the system and thereby enabling formation of a new chemical bond between the material and the CO_2. In contrast to previous methods, the kinetics of uptake and release can be controlled by manipulating a simple physical variable - the charge in the material – since CO_2 capture/release occurs spontaneously once extra electrons are introduced or removed. Furthermore, the need for a temperature swing and the associated energy cost can in some embodiments be obviated.

Example 1A: N-doped graphitic carbon as in Figure 1(a)

The adsorption energies for a single CO_2 molecule on the N-doped graphene model of Figure 1(a) were calculated for different added charges and present the results in (b)-(f). With $2e^-$ added to the supercell the CO_2 still resides at the N site with little change in adsorption energy. With $4e^-$ added, both the N site and the adjacent C site have stable CO_2 binding structures, although the C-site complex is already significantly more strongly bound. With $6e^-$ added, chemisorption of CO_2 to the adjacent C site dominates, with no stable N-site adsorption being found. It is also important to note that the chemisorption occurs at the C site adjacent to the N dopant. This is to be expected: since they have lost electron density to the neighbouring (more electronegative) N atom, it is these carbons that are “activated” to accumulate the additional charge when it is supplied and bind with CO_2.

Example 1B: The graphitic carbon nitride

Embodiments of graphitic carbon nitride include g-C_4N_3 and g-C_3N_4, g-C_2N and g-CN. Illustrative embodiments of these four structures are seen in Figure 1(h), Figure 1(j), Figure 1(k) and Figure 1(m), respectively. Band structure calculations show that g-C_4N_3 is half-metallic while g-C_3N_4 is a semiconductor with the indirect band gap of 1.87 eV. g-C_2N and g-

CN are also predicted to be semiconductors with bandgaps less than 2eV, although experimentally bandgaps tend to be somewhat larger than the values predicted with DFT.

In Figures 1(h)-(m), the darker balls represent nitrogen atoms and the lighter balls represent carbon atoms. The unit cell for each of g-C_4N_3 and g-C_3N_4, g-C_2N and g-CN (Figure 1(h)-(m)) are indicated by the dark dashed lines. In the embodiments shown in Figures 1(h) and 1(j), the unit cell is repeated four times for form a graphitic nanosheet, represented by the light dashed line. However, the scope of the disclosure is not limited to 4 unit cells and a plurality of unit cells can be used to form nanosheets of indefinite dimensions along a 2D plane.

Although not shown in Figure 1, the unit cell can be used to construct structures such as fullerenes, and these structures can be used to form higher order structures. In the case of the graphitic nanosheets from Figure 1, these structures can be arranged into a graphene-type structure where the nanosheets are arranged to be stacked on top of one another along a z direction. Different structures, such as nanotubes and/or fullerenes may be interlaced between the stacked nanosheets. If additional heteroatoms, such as B, S, O and Si, and metals such as Li, Mg, Ge and Al are included into or associated with the graphitic nanosheets, then the unit cell will adopt a different structure. In Figure 1h, C_1 and C_2 denote different C atoms in g-C_4N_3 unit cell, and in Figure 1j N_1, N_2 and N_3 denote different N atoms in g-C_3N_4 unit cell.

Example 1C: B-doped graphene

Figure 9 shows the electronic structures of B-doped graphene nanosheets with increasing boron content, i.e., BC_{49} (Figure 9a) BC_7 (Figure 9b), BC_5 (Figure 9c) and BC_3 (Figure 9d), and details the lowest-energy configurations and the calculated band structures of these B-doped graphene nanosheets. The light and dark grey balls represent B and C atoms, respectively, and the unit cells of each B-doped graphene are indicated by black dot lines. The dashed horizontal line denotes the Fermi level in the respective eV level graphs for each type of B-doped graphene. The calculations indicate that B-doped graphene with B content ranging from 0–16.7 atom % has good electrical conductivity and high electron mobility, which should readily facilitate charge/electron injection/release for charge-controlled switchable hydrogen storage.

Example 2: Use of the material

H_2 adsorption/desorption

Single H_2 Molecule Adsorption on Neutral and Negatively Charged g-C_4N_3 Nanosheets.

For the neutral case, the H_2 molecule exhibits weak interaction with g-C_4N_3 with small adsorption energy of 0.08 eV. After injection of three extra electrons into the g-C_4N_3 supercell with a general structure of that shown in Figure 1h, the electrostatic interactions between the adsorbed H_2 molecule and the $3e^-$ negatively charged g-C_4N_3 are greatly enhanced, with the adsorption energy of the H_2 molecule increasing to 0.50 eV. Compared with the configuration of the H_2 molecule on neutral g-C_4N_3, the perpendicularly aligned H_2 molecule resides close to the top of one N atom of the $3e^-$ negatively charged g-C_4N_3.

To study the effects of charge state on a H_2 molecule adsorption on g-C_4N_3 sheets, the H–H bond length, the distance between N atom and H_2 molecule, the induced dipole moment of H_2 molecule, and the adsorption energy of H_2 molecule as a function of the charge state were plotted in Figure 2. The results show that the H–H bond length and the dipole moment of the H_2 molecule increase dramatically with increasing injection electrons. This is because the electric field generated near the surface of the charged g-C_4N_3 is increased as the density of injected electrons increases. Simultaneously, the distance between the H_2 molecule and the N atom of g-C_4N_3 decreases significantly as the density of injected electrons increases. When four electrons are injected into the g-C_4N_3 supercell, the H_2 molecule is predicted to dissociate and atomically bond to the negatively charged g-C_4N_3, indicating that molecular hydrogen adsorption can be achieved only below a certain critical injected charge density. For the $2e^-$ and $3e^-$ negatively charged g-C_4N_3 supercells, the adsorption energies of a H_2 molecule are 0.25 and 0.50 eV, respectively. These values show that negatively charged g-C_4N_3 can be an excellent media for hydrogen storage.

In Figure 3a, the lowest-energy configuration of neutral g-C_4N_3 with a weakly bounded H_2 molecule is shown. Three electrons are then added to the neutral g-C_4N_3, and the system relaxes to the $3e^-$ negatively charged optimized state. In Figure 3b, the lowest-energy configuration of the 3e- negatively charged g-C_4N_3 with a strongly bounded H_2 molecule is shown. Three electrons are removed, and then the system is allowed to relax, forming a weakly bonded H_2 molecule. When three extra electrons are introduced into g-C_4N_3, the interactions between the H_2 molecule and the $3e^-$ negatively charged g-C_4N_3 are significantly larger than that with neutral g-C_4N_3, and the H_2 molecule spontaneously became strongly bound with adsorption energy 0.50 eV. This process is exothermic by 1.21 eV without any energy barrier. On the other hand, when three extra electrons are removed from the $3e^-$ negatively charged g-C_4N_3, the H_2 molecule spontaneously return to the weakly bound state and desorb from g-C_4N_3. This process is exothermic by 1.22 eV without any energy barrier. Therefore, the hydrogen storage/release processes on negatively charged g-C_4N_3 is reversible with fast kinetics, and can be easily controlled via adding/removing the extra electrons.

The Capacity of Hydrogen Storage on Negatively Charged g-C_4N_3 Nanosheets

In Figure 4a, the $3e^-$ negatively charged g-C_4N_3 can adsorb up to 12 H_2 molecules with average adsorption energy slightly decreased from 0.50 (n=1) to 0.31 eV (n=12). This reduction in average adsorption energy is likely due to the steric hindrance effect among the adsorbed H_2 molecules. Further increase the number of H_2 molecules (n>12) leads to significant decrease of the average adsorption energy of H_2 molecules, therefore, n=12 is the likely saturation or full hydrogen coverage. At the full hydrogen coverage on $3e^-$ negatively charged g-C_4N_3, the average adsorption energy of H_2 molecules, 0.31 eV/H_2.The corresponding gravimetric density of stored hydrogen is 6.3 wt%. The average adsorption energies of H_2 molecules were calculated on different negatively charged g-C_4N_3 at full hydrogen coverage, Figure 4b. In a progression similar to the case of a single adsorbed H_2 molecule (Figure 2d), the average adsorption energy of H_2 molecules at full hydrogen coverage increases from 0.08 eV/H_2 on neutral g-C_4N_3 to 0.31 eV/H_2 on $3e^-$ negatively charged g-C_4N_3.

The Capacity of Hydrogen Storage on Neutral and Negatively Charged g-C_3N_4 Nanosheets.

For g-C_3N_4 sheet, the interactions between H_2 molecules and negatively charged g-C_3N_4 exhibit the similar behaviour. Here, the negatively charged g-C_3N_4 can adsorb up to 14 H_2 molecules with small average adsorption energy decrease, and the configuration of adsorbent with 14 H_2 molecules was defined full hydrogen coverage. On neutral g-C_3N_4, the H_2 molecules are weakly adsorbed with a small adsorption energy of 0.10 eV/H_2, while the average adsorption energy of H_2 molecules increases from 0.10 eV/H_2 on neutral g-C_3N_4 to 0.25 eV/H_2 on $3e^-$ negatively charged g-C_3N_4.These results indicate that the hydrogen adsorption/desorption processes on negatively charged g-C_3N_4 can be simply controlled and reverse by switching on/off the charges state of g-C_3N_4. The corresponding gravimetric density was 7.1 wt% H_2.

The Capacity of Hydrogen Storage on Neutral and Positively Charged BC_{49} nano-sheets.

All the adsorption sites were examined: directly on top of a C or B atom, above the midpoint of a bond linking the C and B atoms, and above the centre of a honeycomb-like hexagon. The top of B atom is the most stable site both for neutral and positively charged cases. Figure 10 shows the lowest-energy configurations of a H_2 molecule absorbed on neutral and 5e positively charged BC_{49} (corresponding to the charge density of 3.82×1014 cm^{-2} as defined in *Tan et al., Sci. Rep. 2015, 5, 17636*). On neutral BC_{49} (Figure 10(a)), the H_2 molecule aligns perpendicular to BC_{49} nanosheet and on top of the doped B atom. The distance between the H_2 molecule and B atom is 2.760 Å, and the H-H bond length is 0.753

Å which is similar to isolated H_2 molecule (0.752 Å from our calculation). Mulliken population analysis suggests that the amount of transferred electron from BC_{49} to absorbed H_2 is negligible (about 0.001 e-). For the neutral case, the H_2 molecule exhibits a weak interaction with BC_{49} with an adsorption energy of 0.06 eV.

After injecting five extra positive charges into the BC_{49} unit cell (Figure 10(b)) i.e. by removing 5 electrons, the electrostatic interactions between the adsorbed H_2 molecule and the 5e positively charged BC_{49} were greatly enhanced, and the adsorption energy increased to 0.79 eV. Compared with the configuration of the H_2 molecule on neutral BC_{49}, the distance between the perpendicularly aligned H_2 molecule and B atom shortens from 2.760 to 1.593 Å, and the H-H bond length elongates from 0.753 to 0.813 Å. Mulliken population analysis suggests that the extra positive charges transferred from BC_{49} to the absorbed H_2 molecule is significantly increased from -0.001 to 0.331 e. More importantly, we note that the lower H atom is negatively charged (-0.064 e), whereas the charge on the upper one is positive (+0.395 e), indicating that the electrons of the H_2 molecule are polarized.

In order to explore the underlying mechanism of the enhanced adsorption of a H_2 molecule onto positively charged BC_{49}, the electron density distributions of the frontier orbitals (i.e., the highest occupied molecular orbital (HOMO)) for neutral BC_{49} nanosheet were plotted. Figure 11(a) shows the isosurface (0.06 e/au) of HOMO of neutral BC_{49}. The shades of the orbitals show the wave function of HOMO (lighter, positive; darker, negative). Figure 11(b) shows the differences in electron density distribution of 5e positively charged BC_{49} relative to neutral BC_{49} using frozen atomic geometry. Figure 11(c) shows the differences in electron density distribution of a H_2 molecule adsorbed on 5e positively charged BC_{49} relative to neutral BC_{49} using frozen atomic geometry. In Figure 11(a) and (b), the isosurface values are 2×10^{-6} e/au, and darker and lighter shades refer to the electron-rich and -deficient areas, respectively. The HOMO of neutral BC_{49} is predominantly distributed on the doped B atom, which suggests that when an electron is extracted from the neutral BC_{49}, the extracted electron is from p orbitals of B atom of the BC_{49}. This is further confirmed by comparison of the difference in electron density distribution of 5e positively charged BC_{49} relative to neutral BC_{49}, as shown in Figure 11(b). From Figure 11(b), it can be seen that when 5 electrons are extracted from the neutral BC_{49}, the positive charges spread across the B atom of the BC_{49}, and generate a high electric field near the surface of the positively charged BC_{49} (*Yoon et al., Nano Lett. 2007, 7, 2578–2583*), resulting in polarization of the adsorbed H_2 molecule (as shown in Figure 11(c)), and greatly enhance the adsorption of H_2 molecule on the positively charged BC_{49}.

The adsorption energy of the H_2 molecule, the H-H bond length (R1), the induced dipole moment of the H_2 molecule, and the distance between the B atom and the H_2 molecule (R2), as a function of the positive charges, were plotted in Figure 12 to examine the dependence of enhanced H_2 molecular adsorption on positively charged BC_{49} nanosheets. The results show that the H-H bond length (Figure 12(b)) and the dipole moment of the H_2 molecule (Figure 12(c)) increase dramatically with increasing number of positive charges. This is because the electric field generated near the surface of the positive charged BC_{49} increased as the density of positive charges increased. Simultaneously, the distance between the H_2 molecule and the B atom of BC_{49} decreased significantly as the density of positive charges increased, as shown in Figure 12(d). When nine positive charges were introduced into the BC_{49} unit cell, the H_2 molecule was predicted to dissociate and atomically bond to the positively charged BC_{49}, indicating that molecular H_2 adsorption can be achieved only below a certain critical introduced positive charge density. For the 3e, 4e and 5e positively charged BC_{49}, the adsorption energies of a H_2 molecule are 0.20, 0.41 and 0.79 eV, respectively, which are much larger than the optimal adsorption energy for H_2 on high-performance adsorbents (0.1–0.2 eV) (*Zhou et al., Proc. Natl. Acad. Sci. USA 2010, 107, 2801–2806; Liu et al., Appl. Phys. Lett. 2010, 96, 123101*) indicating that positively charged B-doped graphene can be excellent media for hydrogen storage.

The energy change of a H_2 molecule adsorbed on BC_{49} after introduction or removal of five extra positive charges was studied, as shown in Figure 13, to investigate the reversibility of hydrogen storage/release on the 5e positively charged BC_{49},. Figure 13(a) depicts the lowest-energy configuration of neutral BC_{49} with a weakly bounded H_2 molecule. Five positive charges were added to the neutral BC_{49}, and Figure 13(a) shows the change in energy as the system relaxed to the 5e positively charged optimized state. Figure 13b depicts the lowest-energy configuration of 5e positively charged BC_{49} having a strongly bounded H_2 molecule. Five extra positive charges were removed, and the system was allowed to relax, forming a weakly bound H_2 molecule. When five extra positive charges were introduced into neutral BC_{49}, the interactions between the H_2 molecule and the 5e positively charged BC_{49} increased significantly, and the H_2 molecule spontaneously bound with an adsorption energy of 0.79 eV; this process was exothermic by 0.36 eV. On the other hand, when five extra positive charges were removed from 5e positively charged BC_{49}, the H_2 molecule spontaneously returned to the weakly bound state and desorbed from BC_{49}; this process was exothermic by 0.83 eV. Therefore, the hydrogen storage/release processes on positively charged BC_{49} are reversible with fast kinetics, and can be easily controlled by adding/removing the extra positive charges.

The maximal number of absorbed H_2 molecules on each B atom of B-doped graphene

In order to study the maximal number of absorbed H_2 molecules on each B atom of B-doped graphene, the average adsorption energy of H_2 molecules on 5e positively charged BC_{49} was studied by increasing the number of adsorbed H_2 molecules, and found that each B atom can storage up to two H_2 molecules, which was located on both sides of B-doped graphene with average adsorption energy of 0.51 eV/H_2, as shown in Figure 14(a). Further increases the number of H_2 molecules (more than two H_2 molecules) led to a significant decrease in the average adsorption energy of H_2 molecules. Therefore, the maximal number of H_2 molecules that can be electrocatalytically adsorbed on each B atom is two. Moreover, the average adsorption energies of the positively charged BC49 with two adsorbed H2 molecules was calculated as a function of the positive charges, as shown in Figure 14(b). Similar to the case of a single adsorbed H_2 molecule, the average adsorption energy of H_2 molecules increases continuously from 0.06 eV/H_2 on neutral BC_{49} to 0.51 eV/H_2 on 5e positively charged BC_{49}.

The capacity of hydrogen storage on positively charged BC5

Since the B atoms are the active sites for electrocatalytically hydrogen storage, the B content can determine the capacity of hydrogen storage on positively charged B-doped graphene. BC_5 nanosheet, which has the highest B content among all the conductive B-doped graphene, was studied to determine the capacity of hydrogen storage on positively B-doped graphene. Figure 15(a) and (b) show the lowest-energy configurations of neutral and 0.8e positively charged BC_5 with two H_2 molecules adsorption on each B atom. The interaction between H_2 molecules and positively charged BC5 exhibit the similar behaviour as that of positively charged BC_{49}, as shown in Figure 15(c). The charge density of 0.8e positively charged BC_5 is 4.77×1014 cm^{-2} as defined in *Tan et al., Sci. Rep. 2015, 5, 17636*. On neutral BC_5 (Figure 15(a)), the H_2 molecules are weakly adsorbed with small average adsorption energy of 0.06 eV/H_2, while the average adsorption energy per H_2 molecule increases to 0.58 eV on 0.8e positively charged BC_5 (Figure 15(b)), which is larger than the optimal adsorption energy for H_2 on high-performance adsorbents (0.1–0.2 eV) (*Zhou et al., Proc. Natl. Acad. Sci. USA 2010, 107, 2801–2806; Liu et al., Appl. Phys. Lett. 2010, 96, 123101*). The corresponding gravimetric density of stored hydrogen is up to 5.3 wt%, indicating positively charged BC_5 may be an ideal material for electrocatalytically switchable and high-capacity hydrogen storage. Though H_2 uptake wt% of positively charged BC_5 is slightly less than the target set by U.S. DOE (5.5 wt%), it is important to bear in mind that there are very few materials which can meet the target and operate reversibly under mild conditions. In addition, many chemical hydrogen storage systems use solvents, which significantly decrease the effective weight percent of H_2 production or delivery as one has to take into consideration the weight of the solvent.

Capacity of CO_2 adsorption on negatively charged graphitic carbon nitride and N-doped graphene

The maximum number of captured CO_2 for each negatively charged g-C_4N_3 was determined with different charge density by gradually increasing the number of CO_2 molecules on negatively charged g-C_4N_3 until no more CO_2 can be absorbed, see for example Figure 5. The average adsorption energy of captured CO_2 is calculated as the total adsorption energy divided by the maximum number of captured CO_2. No CO_2 molecules can be captured by negatively charged g-C_4N_3 with small charge density (≤ 12.3×10^{13} cm^{-2}). As the charge density increase from 18.5×10^{13} to 61.6×10^{13} cm^{-2}, the negatively charged g-C_4N_3 can capture two, four and six CO_2 molecules with the average adsorption energy of captured CO_2 molecules ranging from 0.72 to 3.58 eV. A further increase in the number of CO_2 molecules leads to some CO_2 molecules moving far away from the adsorbent during the geometry optimization even if the charge density of g-C_4N_3 is increased further. Therefore, six CO_2 molecules are defined in each 4 unit cell nanosheet of Figure 1h (i.e. CO_2 capture capacity 73.9×10^{13} cm^{-2}) as the likely saturation CO_2 capture coverage.

Substitutional N-doped graphene is conductive and is herein predicted to have electro-responsive switchable binding capacity for CO_2, via the C sites adjacent to the N dopant atoms. Given that there is a limit to the fraction of N that can be doped into graphene of around 1/3, it is also significant to consider the binding capacity for CO_2 around the N site. There are three adjacent carbons that could potentially bind. Indeed, the calculations indicate that each of them can chemisorb a CO_2 molecule once the extra negative charge is introduced. Under the same charging conditions, three CO_2 can adsorb to the neighbouring carbons (optimally two above the plane and one below) as shown in Figure 7, with average adsorption energy -1.81eV per molecule. At the doping fraction indicated in Figure 1(a) (i.e., 1.6wt% of nitrogen), which is very conservative, this would yield a CO_2 binding capacity of *ca.* 13wt%.

Selectivity of adsorption

The adsorption energies of CH_4, H_2 and N_2 were calculated on neutral and negatively charged g-C_4N_3 and compared with those of CO_2. In Figure 6, the comparative adsorption energies of CO_2, CH_4, H_2 H20 and N_2 on neutral, $1e^-$ and $2e^-$ negatively charged g-C_4N_3 are shown. The adsorptions of CH_4, H_2 and N_2 on neutral, $1e^-$ and $2e^-$ g-C_4N_3 are all physical rather than chemical. The distance between the carbon atom of CH_4 (the hydrogen atom of H2, the nitrogen atom of N2) and g-C_4N_3 is 3.157-3.159 (2.111-2.539, 2.865-3.236) Å, respectively. The adsorption energies of CH_4, H_2 and N_2 on neutral, 1 e- and 2 e- g-C_4N_3 range from 0.06 to 0.39 eV. In contrast, although CO_2 is physically adsorbed at neutral and

$1e^-$ g-C_4N_3 with small adsorption energy in the range from 0.24 to 0.32 eV, CO_2 is tightly chemisorbed on $2e^-$ g-C_4N_3 with large adsorption energy of 1.20 eV. The above comparisons demonstrate that negatively charged g-C_4N_3 has very high selectivity for capturing CO_2 from CH_4, H_2 and/or N_2 mixtures.

Figure 8 compares the adsorption energies of CO_2, CH_4, H_2, N_2 and H_2O on neutral, 4e- and 6e- negatively charged N-doped graphene of Figure 1. At the intermediate charge of 4e-, both CO_2 and H_2O are favourably bound in comparison with the other gases. However, at the highest charge 6e- CO_2 is strongly favoured over all the other gases. This implies that the N-doped graphene material could show superior selectivity for CO_2 binding – particularly for capturing CO_2 out of a gas stream containing water.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

Any journal articles referred to herein are incorporated by reference in their entirety, but this disclosure takes precedence if there is any conflicting information. It is to be understood that, if any prior art publication is referred to herein such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

Claims

1. A method of adsorbing gas from a gas stream, the method comprising the steps of:

providing a gas permeable graphitic material comprising carbon and at least one other element;

allowing a gas to contact the graphitic material;

applying a first potential to the graphitic material to adsorb at least some of the gas thereby producing a gas loaded graphitic material; and

applying a second potential to the gas loaded graphitic material to desorb at least some of the gas.

2. The method of claim 1, wherein the at least one other element is nitrogen and the graphitic material is carbon nitride and/or nitrogen-doped graphene.

3. The method of claim 1, wherein the at least one other element is boron and the material is boron-doped graphene.

4. The method of claim 1 or 2, wherein the first applied potential is less than about 10 volts.

5. The method of any one of the preceding claims, wherein the second potential is applied at room temperature to desorb at least some of the gas.

6. The method of any one of the preceding claims, wherein the gas that contacts the graphitic material comprises hydrogen which is adsorbed in its molecular form.

7. The method of claim 6, wherein following application of the first potential, the gas loaded material comprises more than about 5 wt% gas.

8. The method of any one of the preceding claims, wherein the gas that contacts the graphitic material comprises carbon dioxide which is adsorbed in its molecular form.

9. The method of any one of the preceding claims, wherein the step of allowing the gas to contact the material comprises flowing a gas over nano-sheets of the material.

10. The method of any one of the preceding claims, wherein the first and second potentials are applied sequentially using one or more electrical sources in electrical contact with the graphitic material.

11. The method of any one of the preceding claims, wherein the graphitic material is associated with a layer of an electrically conductive substance and the first and second potentials are applied to the layer.

12. An electrically conductive or semi-conductive adsorbent comprising a gas permeable graphitic material comprising carbon and at least one other element, when used under the influence of an electrical potential to adsorb a gas.

13. The adsorbent of claim 12 wherein the at least one other element is nitrogen.

14. The adsorbent of claim 13, wherein the graphitic material is a graphitic C-N material having a band gap less than about 2.5 eV.

15. The adsorbent of claim 14, wherein the graphitic C-N material has the formula C_XN_Y, wherein X is ≤5 and Y is ≤5.

16. The adsorbent of claim 13 wherein the graphitic material is nitrogen-doped graphene.

17. The adsorbent of claim 12 wherein the at least one other element is boron.

18. The adsorbent of claim 17 wherein the graphitic material is boron-doped graphene.

19. The adsorbent of any one of claims 12 to 18, comprising at least 5 wt% loaded hydrogen gas.

20. The adsorbent of any one of claims 12 to 19, wherein the adsorbent is associated with a layer of an electrically conductive substance.

21. The adsorbent of claim 20, wherein the layer comprises a mixture of the graphitic material and an electrically conductive material.

22. The adsorbent of claim 20 or 21, wherein the electrically conductive material is carbon black and/or graphene.

23. A system for storing gas in an adsorbent, the system comprising:

a gas permeable graphitic material as defined in any one of claims 12 to 22,

an electrical source which allows the application of a first and second potential to the graphitic material,

wherein at the first potential the gas is adsorbed to the graphitic material thereby producing a gas loaded material, and wherein at the second potential at least some of the gas is desorbed from the gas loaded graphitic material.

24. The system of claim 23, wherein the graphitic material is housed in a voluminous body.

25. The system of claim 23 or 24, wherein the voluminous body comprises pressure sensors to monitor the pressure inside the voluminous body when at least the second potential is applied.

26. The system of any one of claims 23 to 25, wherein the voluminous body comprises pressure relief vales to prevent a pressure from exceeding a predetermined value when at least the second potential is applied.

27. The system of any one of claims 23 to 26, further comprising a computer system having one or more computers to control the applied first potential and second potential.

28. The system of claim 27, wherein the computer system is in communication with the pressure sensors and the electrical system, and wherein the electrical system applies the first potential when the pressure sensor exceeds the predetermined value.

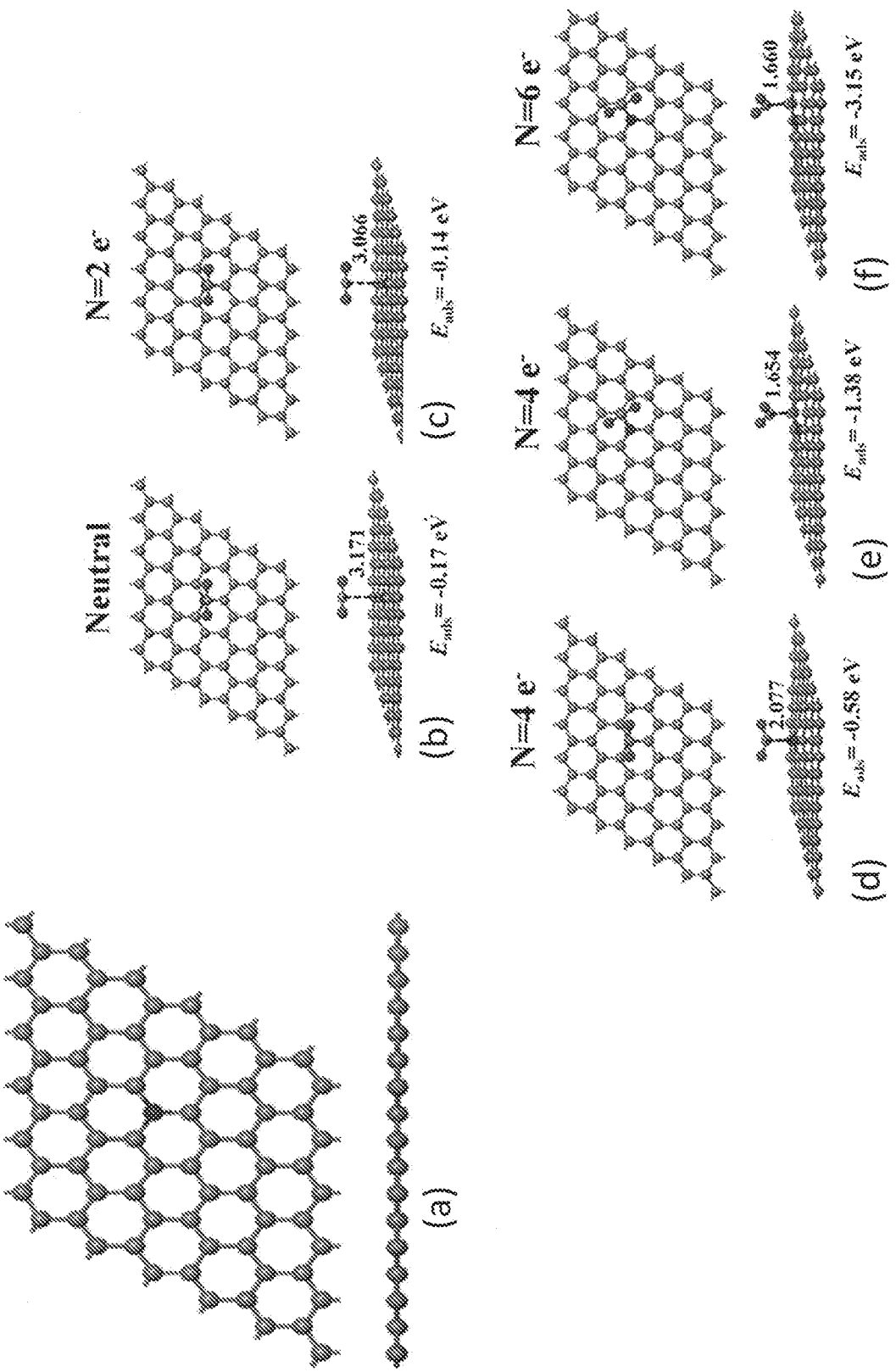
Neutral
N=2 e⁻
N=4 e⁻
N=4 e⁻
N=6 e⁻
3.171
3.066
2.077
1.654
1.660
(a)
(b)
E_{ads} = -0.17 eV
(c)
E_{ads} = -0.14 eV
(d)
E_{ads} = -0.58 eV
(e)
E_{ads} = -1.38 eV
(f)
E_{ads} = -3.15 eV

Figure 1

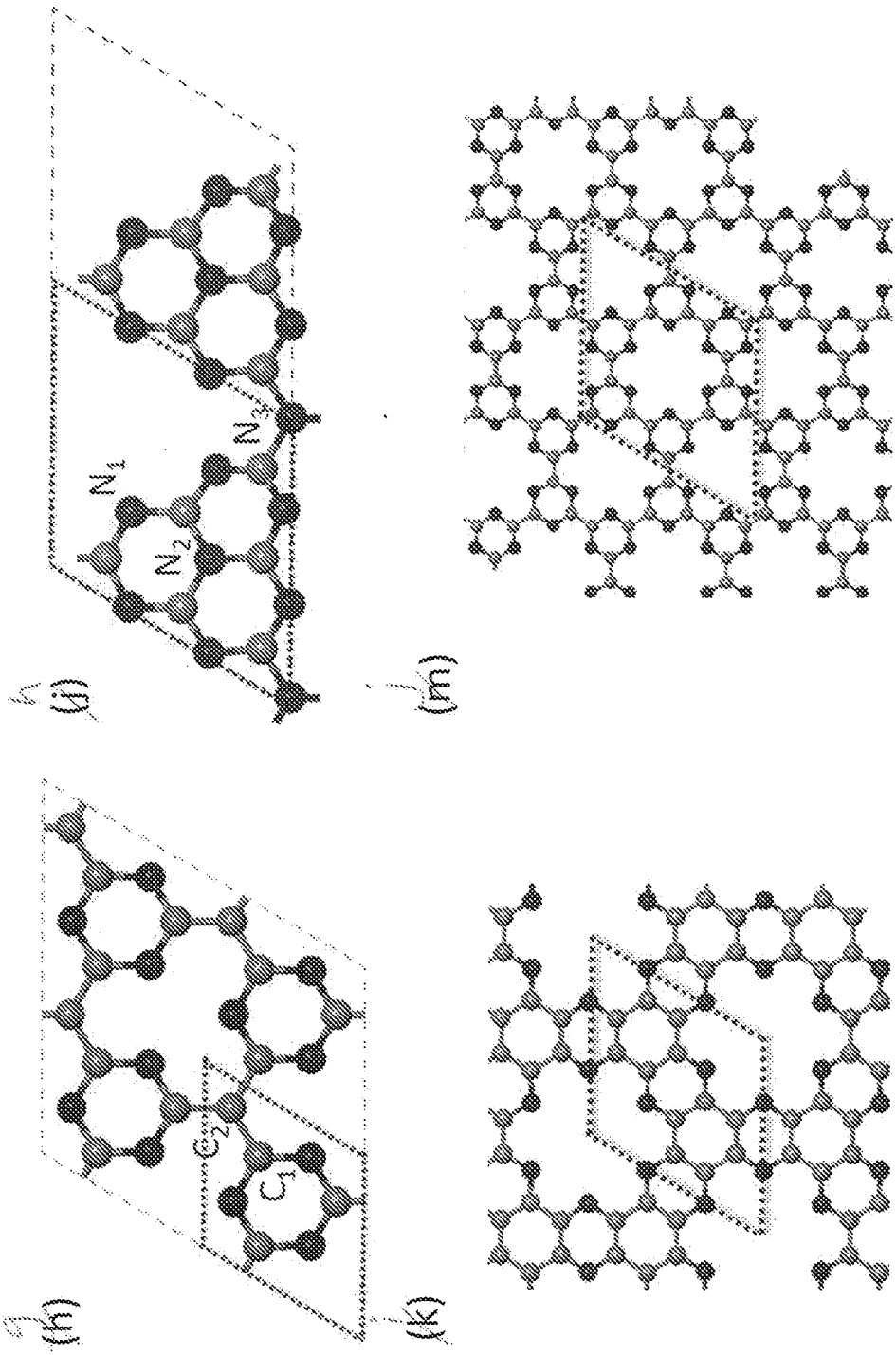

Figure 1 (continued)

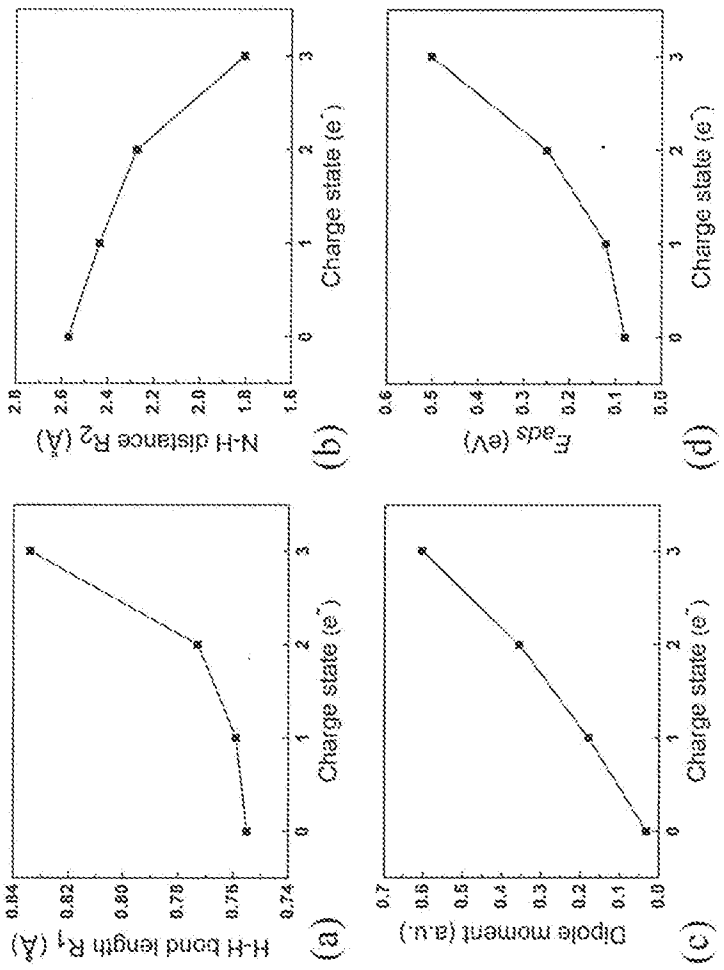
(a)
H-H bond length R_1 (Å)
Charge state (e^-)
(b)
N-H distance R_2 (Å)
Charge state (e^-)
(c)
Dipole moment (a.u.)
Charge state (e^-)
(d)
E_{ads} (eV)
Charge state (e^-)

Figure 2

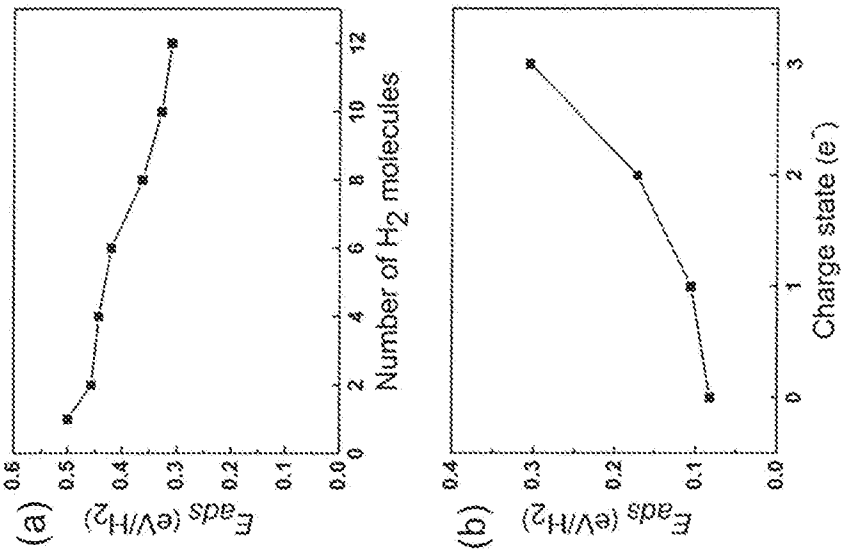

Figure 4

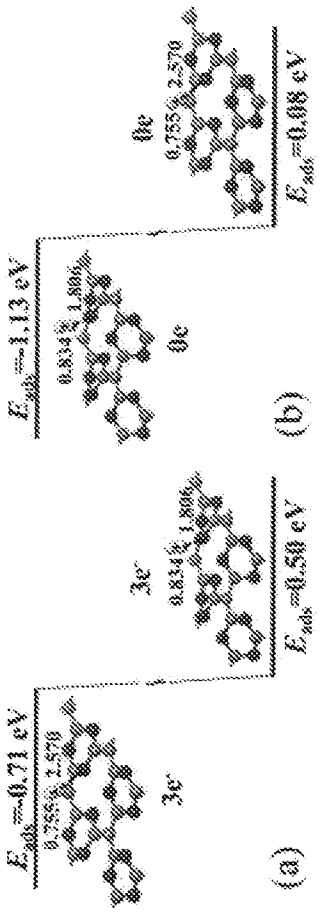

Figure 3

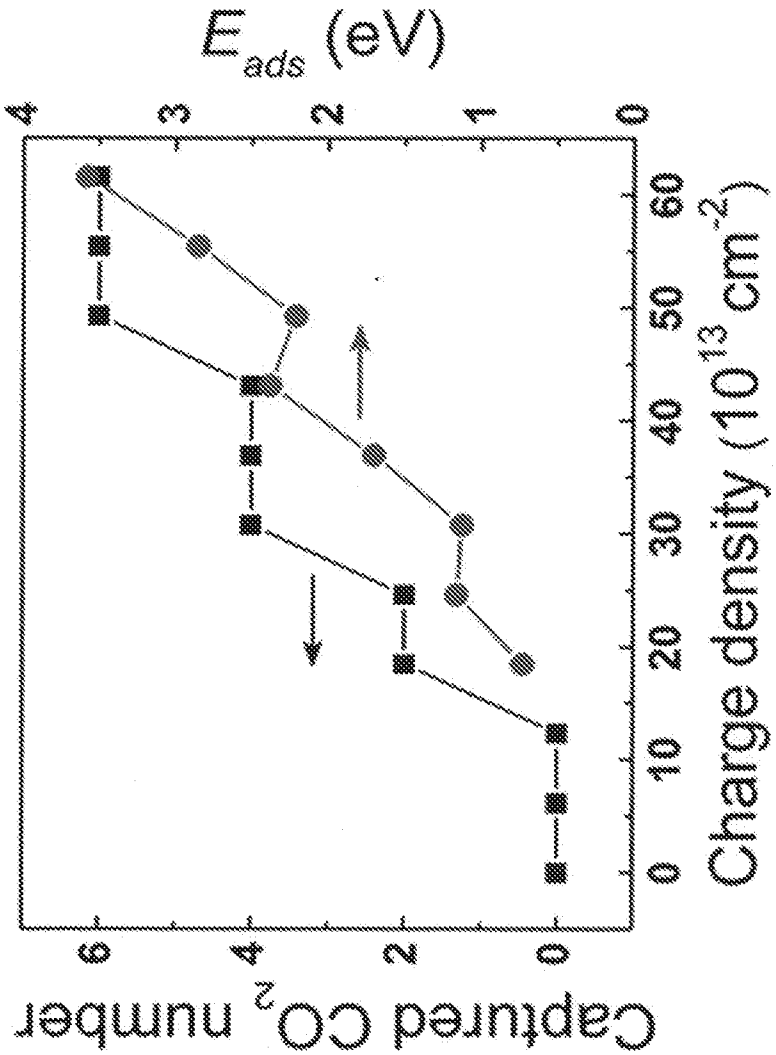
E_{ads} (eV)
4
3
2
1
0
Charge density (10^{13} cm^{-2})
0
10
20
30
40
50
60
Captured CO_2 number
6
4
2
0

Figure 5

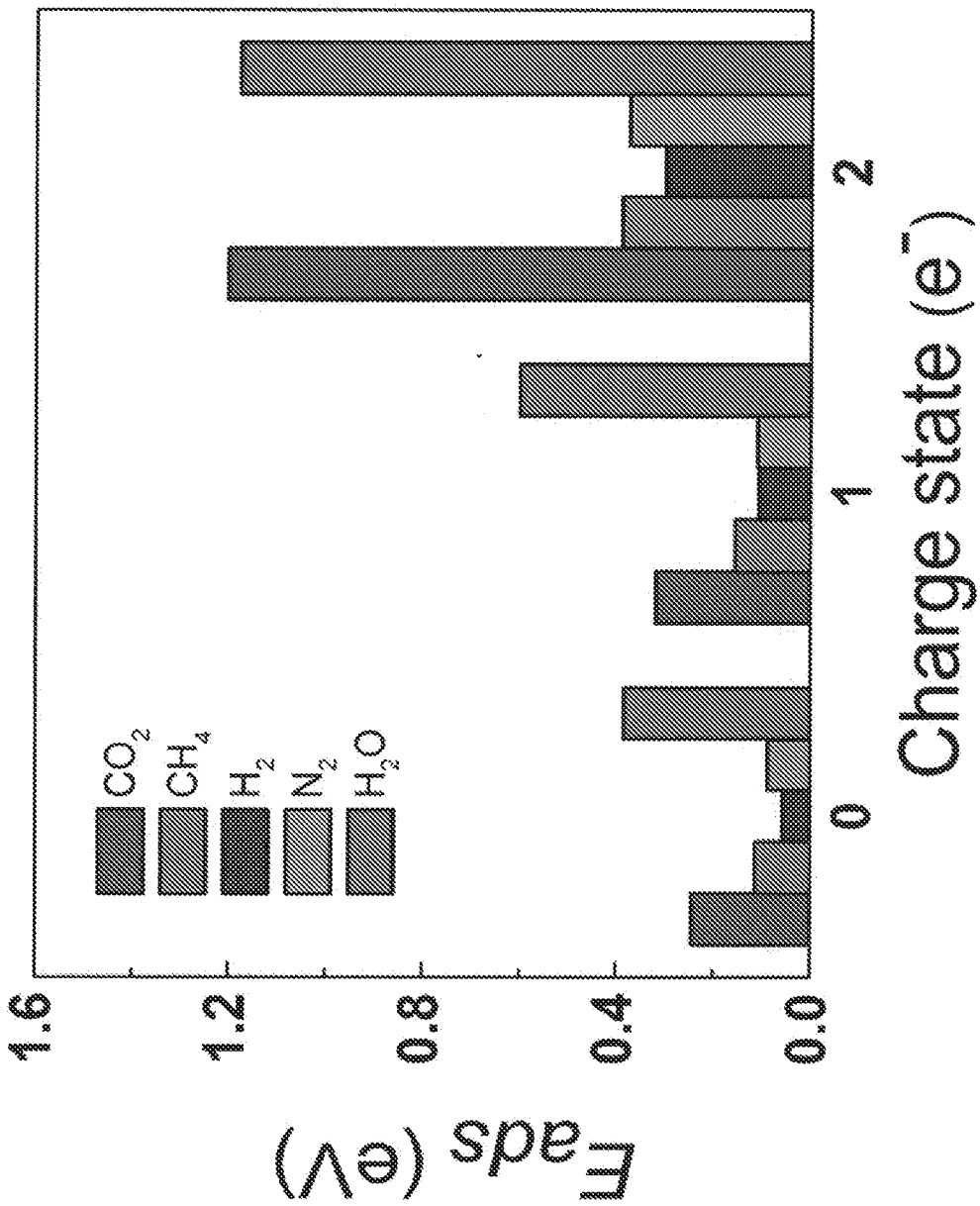

Figure 6

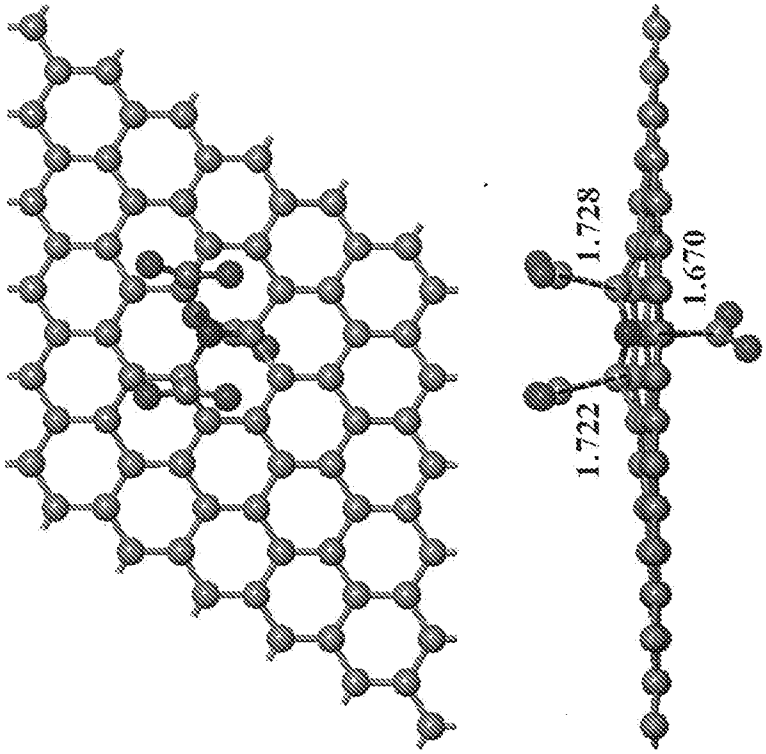

Figure 7

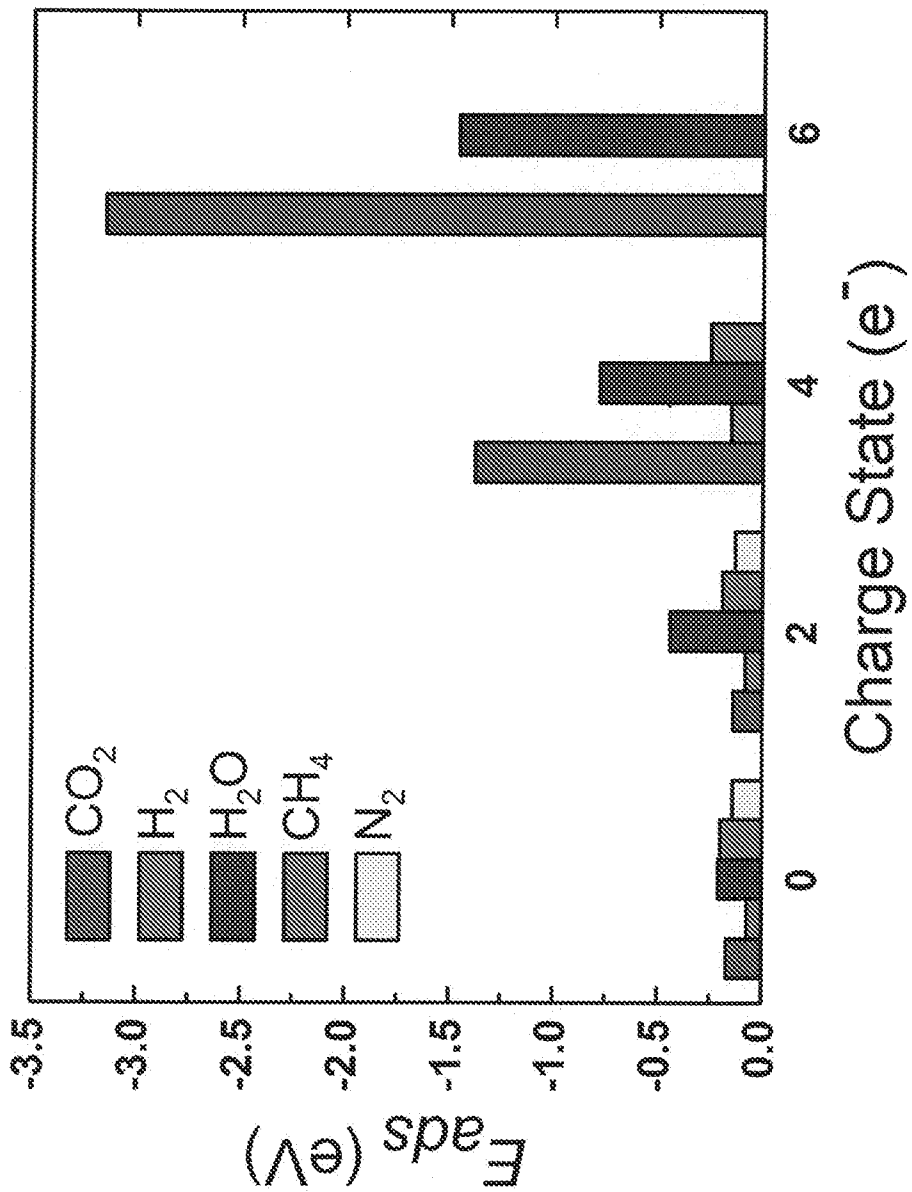
E_{ads} (eV)
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0
2
4
6
Charge State (e^-)
CO_2
H_2
H_2O
CH_4
N_2

Figure 8

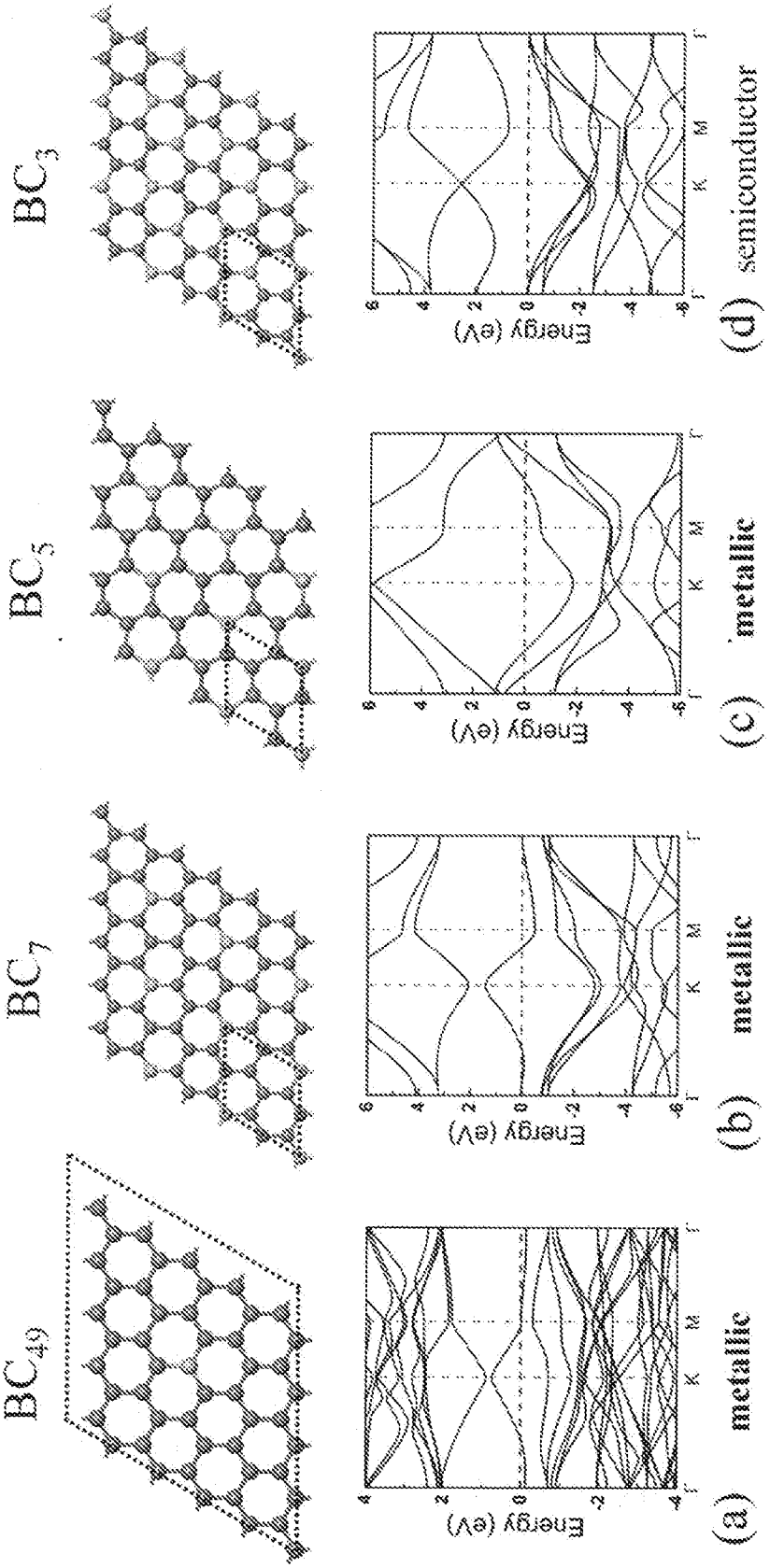
BC49
BC7
BC5
BC3
(a) metallic
(b) metallic
(c) metallic
(d) semiconductor
Energy (eV)
Γ
K
M

Figure 9

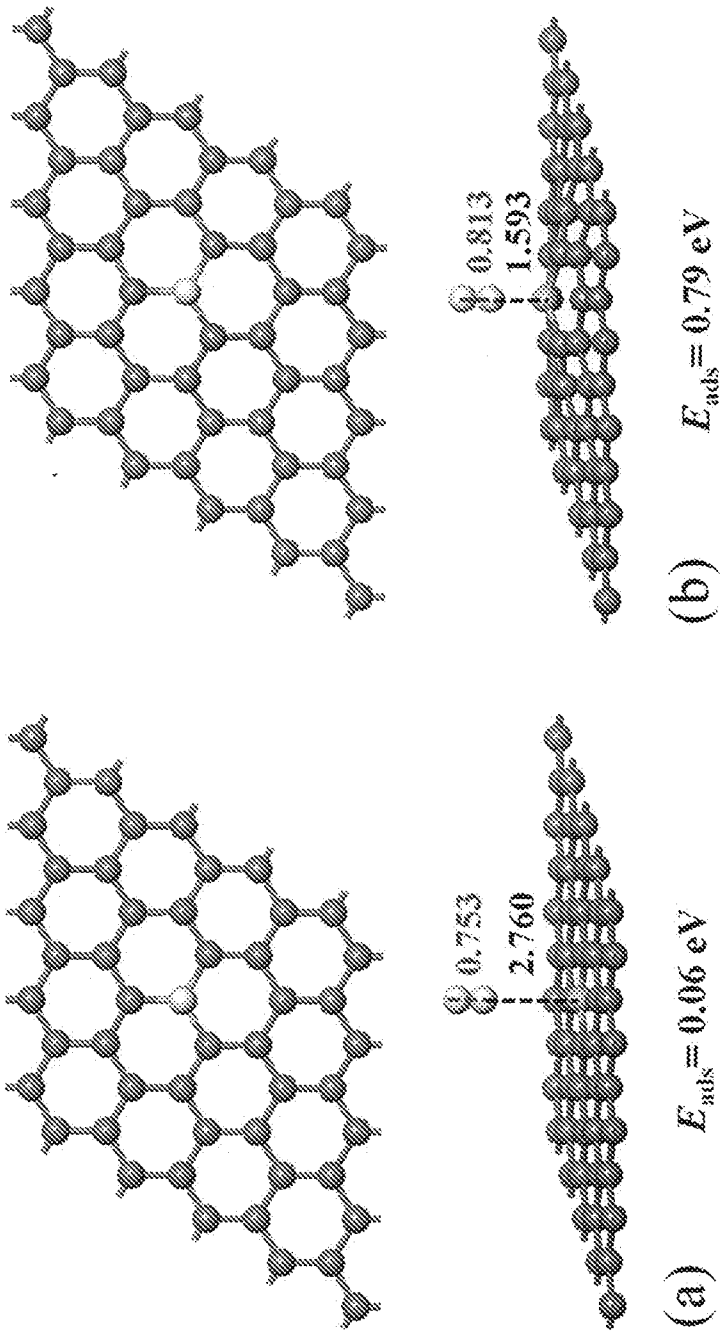

Figure 10

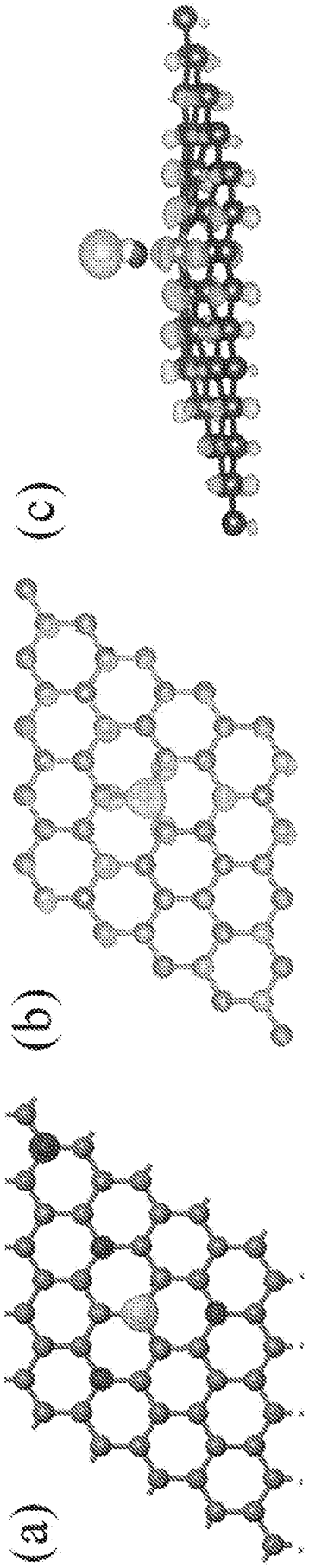

Figure 11

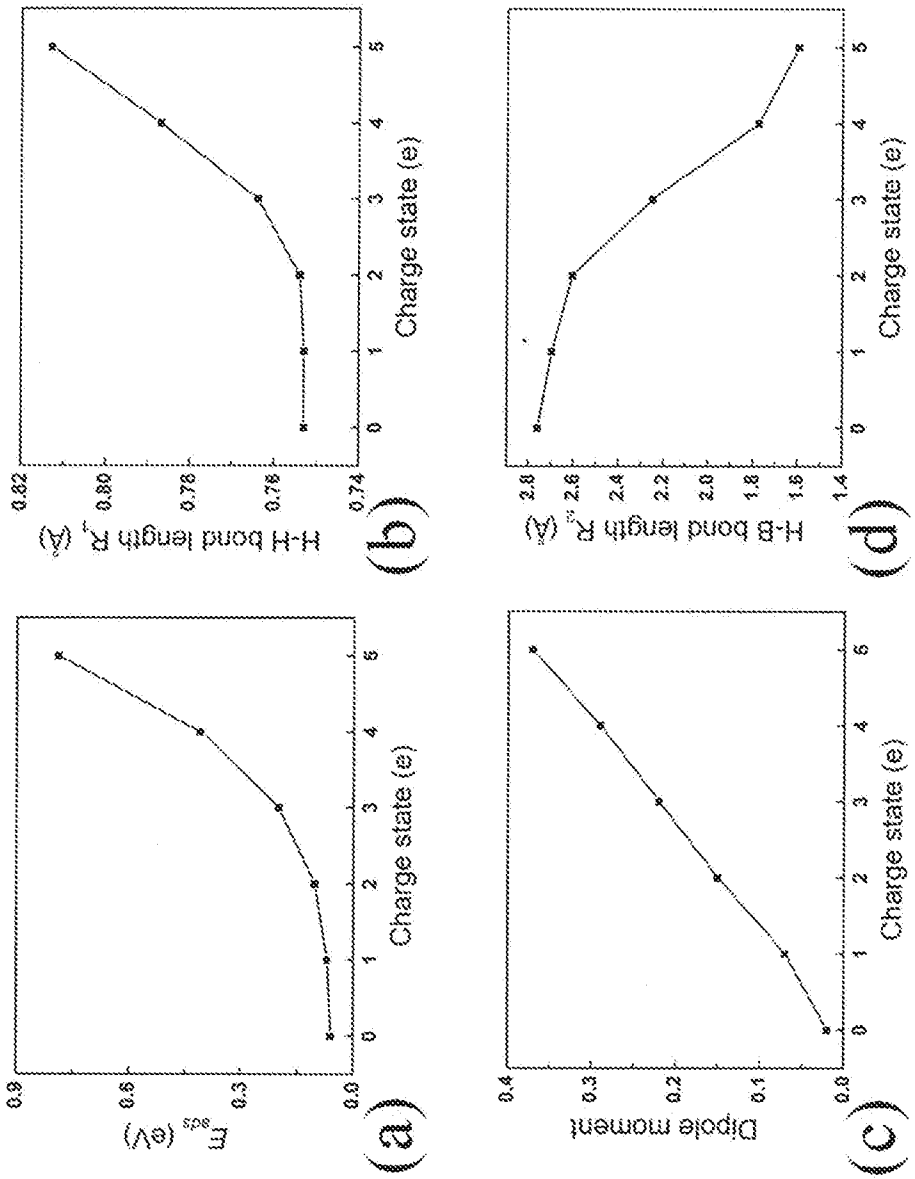
(a)
$E_{F_{ads}}$ (eV)
Charge state (e)
(b)
H-H bond length R_1 (Å)
Charge state (e)
(c)
Dipole moment
Charge state (e)
(d)
H-B bond length R_2 (Å)
Charge state (e)

Figure 12

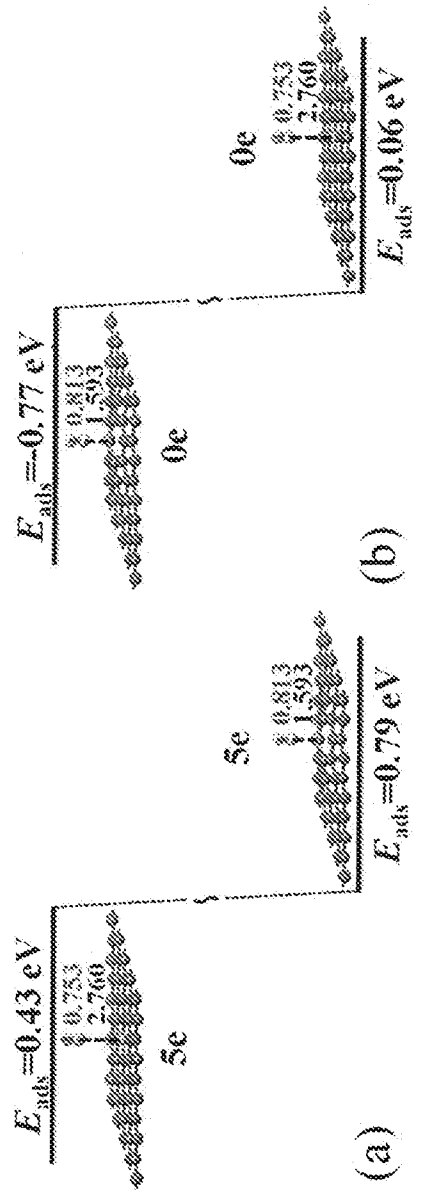

Figure 13

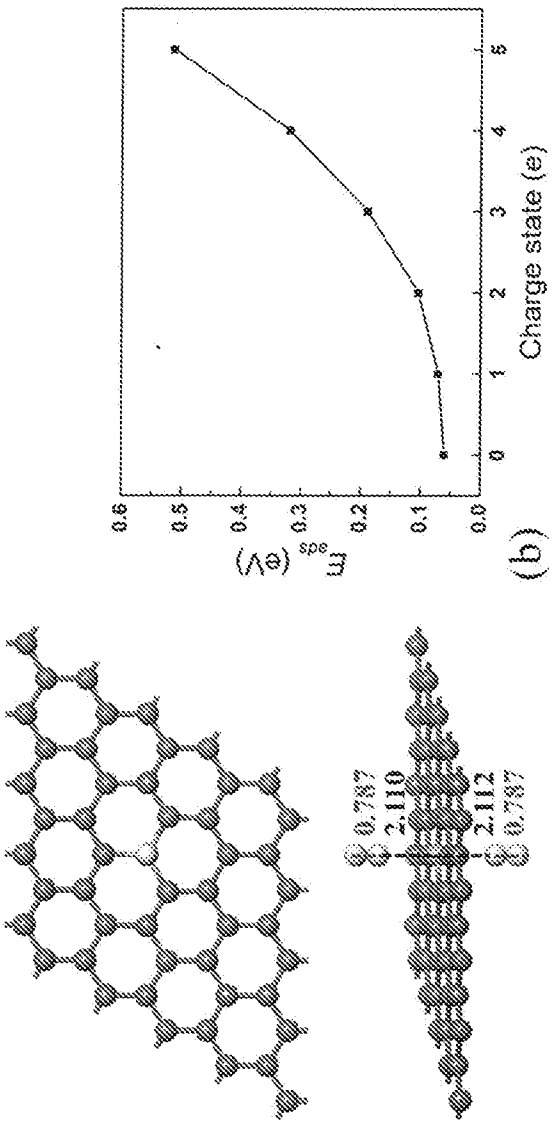

Figure 14

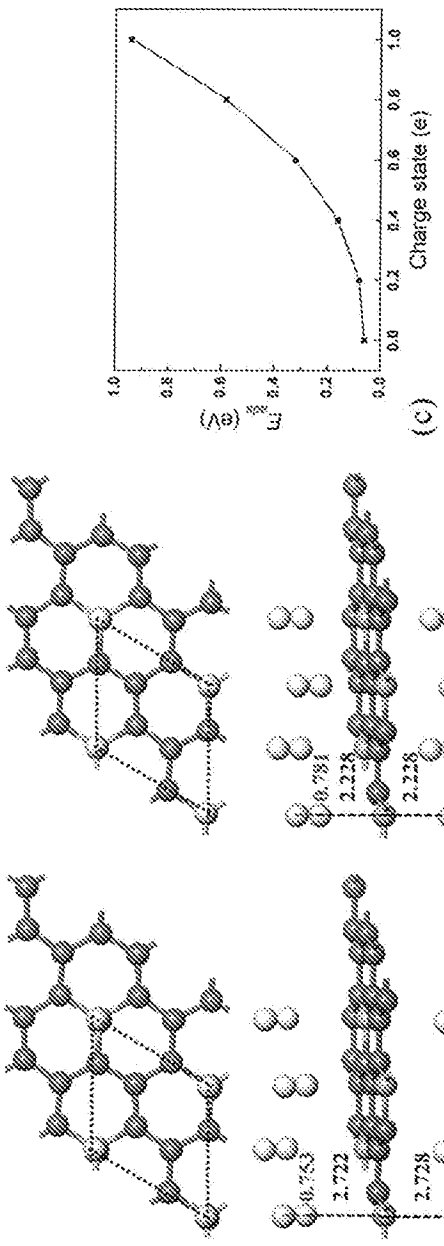

Figure 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2016/050645

A. CLASSIFICATION OF SUBJECT MATTER

B01J 20/20 (2006.01) B01J 20/34 (2006.01) B01D 53/02 (2006.01) B01D 53/32 (2006.01)

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)

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)

EPODOC, WPIAP, Registry, CAPLUS, COMPENDEX, INSPEC, Espacenet, TXTE

Keywords: Sean Smith, Xin Tan, Hassan Tahini, Newsouth Innovations, graphene, graphit+, carbon nitride, boron, nitrogen, dope, substitut+, electric+, gas, storage, hydrogen, carbon dioxide and the like

CPC/IPC: B01D71/02, B01J20/20, B01D2253/102, B01D53/32, B01D53/02, B01D2325/26, B01J2219/08, Y02C10/06, Y02C10/08, Y02C10/10, Y02E60/325, C01B3/0021, B01D2257/504,B01D2257/108, H01M4/133, H01M4/1393, H01M4/583

Applicant/Inventors name searched in internal databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 September 2016	09 September 2016
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Cassandra Mitchell AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832065

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Ao, Z. M. et al. "The electric field as a novel switch for uptake/release of hydrogen for storage in nitrogen doped graphene" Phys. Chem. Chem. Phys., 2012, vol. 14, pg 1463-1467 Table 1, Abstract, Results and Discussion	1-7, 9-28
X	Ao, Z. et al. "Electric field manipulated reversible hydrogen storage in graphene studied by DFT calculations" Phys. Status Solidi A, 2014, vol 211, no. 2, pg 351-356 Abstract, Results and Discussion	1-7, 9-28
X	Ao, Z. M. et al. "Electric field activated hydrogen dissociative adsorption to nitrogen-doped graphene" J. Phys. Chem. C 2010, vol. 114, pg 14503-14509 Abstract, Results and Discussion	1-7, 9-28
X	Tan, X. et al. "Layered Graphene-Hexagonal BN Nanocomposites: Experimentally Feasible Approach to Charge-Induced Switchable CO2 Capture" ChemSusChem; First published 12 June 2015, vol. 8, pg 2987-2993 Figure 7, Results and Discussion, Conclusions	1-3, 8-18, 20-28
X	US 2010/0284903 A1 (HARUTYUNYAN A) 11 November 2010 [0009]-[0045]	1-6, 8-18, 20-28
A	US 2008/0175780 A1 (PEZ G P ET AL) 24 July 2008	

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2016/050645**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2010/0284903 A1	11 November 2010	US 2010284903 A1	11 Nov 2010
		JP 2012526720 A	01 Nov 2012
		JP 5770166 B2	26 Aug 2015
		US 2014194658 A1	10 Jul 2014
		WO 2010132300 A2	18 Nov 2010
US 2008/0175780 A1	24 July 2008	US 2008175780 A1	24 Jul 2008
		WO 2008127749 A2	23 Oct 2008

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.