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(54) Title: MODIFICATION OF CARBON PARTICLES

(57) Abstract: The present invention relates to a process for modifying carbon particles, such as graphites, graphene nanoplatelets, carbon black and other carbons, and to modified carbon particles obtainable by such a process. The process for modifying carbon particles is performed within an apparatus which comprises a sample holder located below a reactive zone and comprises the following steps: a) provision of carbon particles on the sample holder of apparatus, b) fluidizing the carbon particles in apparatus with a gaseous stream into the reactive zone, c) keeping the carbon particles with the gaseous stream in the reactive zone for at least 1 sec and feeding energy of at least 2.4 kJ into the reactive zone, and d) modification of the carbon particles in the reactive zone to obtain modified carbon particles. It is preferred that the carbon particles are modified by a fluidized bed plasma process.



Modification of carbon particles

Description

- 5 The present invention relates to a process for modifying carbon particles, such as graphites, graphene nanoplatelets, carbon black and other carbons, and to modified carbon particles obtainable by such a process.

10 Carbon particles, such as graphites, graphene nanoplatelets, carbon black and other carbons are promising candidates for a wide variety of applications and can be used as bulk active materials, e.g. graphite electrodes in batteries, as bulk support materials e.g. for catalytic applications or as a component of composite materials, such as polymer composites, conductive adhesives, conductive coatings or conductive inks.

15 In recent years, graphene nanoplatelets, as a nanoscale form of carbon with exceptional properties, attract a lot of interest with respect to these applications. Furthermore, it was found that surface modifications, doping or functionalization can significantly improve the performance of a respective carbon material. For a specific application, both the carbon particles themselves as well as the modification, which can
20 be chemical (e.g. doping and/or functionalization) or morphological (e.g. expansion), have to be fine-tuned to achieve the optimum in performance.

One of the most advanced methods to carry out such treatments on granular or powder materials are plasma chemical processes. These processes can be considered as
25 "dry", are very clean, and the reaction products do not need to be isolated from solvents, byproducts or other reactants by tedious separation procedures.

In US-A 2009/0130442, it is disclosed that expanded graphite is derived from a graphitic or partially graphitic starting material. The expanded graphite is obtained by
30 initial reaction of the starting material with substances or mixtures capable of intercalation to give a compound designated as an intercalation compound and subsequent expansion in plasma.

WO 2012/076853 discloses methods of processing particulate carbon material, such as
35 graphitic particles or agglomerates of carbon nanoparticles, such as carbon nanotubes. The starting material is agitated in a treatment vessel in the presence of plasma generated between electrodes, e.g. between a central electrode and an outer rotating conductive drum containing the material to be treated.

40 US 2013/0022530 A1 describes a process for the production of exfoliated graphite, involving providing a graphite intercalation compound and exfoliating the graphite

intercalation compound through a plasma which is of at least 6000°C to bring the graphite intercalation compound to a temperature between about 1600°C and about 3400°C.

- 5 US 2011/0300056 A1 describes a process for production of nano-structures, involving providing a graphite flake comprising graphene layers, intercalating the graphite flake to form a graphite intercalation compound and exfoliating the graphite intercalation compound by exposing it to a temperature between about 1600°C and about 2400°C such that a plurality of individual graphene layers are separated from the graphite
10 intercalation compound.

WO 2008/060703 discloses a process for the production of nano-structures, involving providing a graphite flake comprising graphene layers, intercalating the graphite flake to form a graphite intercalation compound, and exfoliating the graphite intercalation
15 compound under conditions such that a plurality of individual graphene layers are separated from the graphite intercalation compound.

WO 2009/106507 discloses graphite nanoplatelets produced by a process which comprises thermal plasma expansion of intercalated graphite to produce expanded
20 graphite followed by exfoliation of the expanded graphite, where the exfoliation step is selected from ultrasonication, wet milling and controlled cavitation, and where greater than 95% of the graphite nanoplatelets have a thickness of from about 0.34 nm to about 50 nm and a length and width of from about 500 nm to about 50 microns. The plasma reactor can employ a radio frequency induction plasma torch. All three
25 exfoliation methods are performed in an organic solvent or water.

CN-A 103 359 713 discloses a preparation method of graphene which comprises the following steps: introducing protective gas into a reactor of plasma equipment, starting the plasma equipment to generate a plasma in the reactor, adding organic acid
30 intercalated graphite into a reactor and carrying out pyrolysis reaction under the action of plasma to obtain the graphene.

State of the art processes for the morphological and/or chemical modification of graphite, expandable graphite and carbon black are typically designed for one material
35 class only in combination with a specific material treatment, i.e. chemical or morphological modification. For example, intercalated graphite can be expanded in a plasma torch reactor process (see e.g. US 2009/0130442 above). Such processes typically have restrictions in at least one of the following aspects: preparation of the intercalated graphite as starting material, treatment time, treatment energy, possible
40 process gases, number of possible process steps, particles that can be treated and/or source of excitation energy.

Further, in the state of the art these processes either have high power/high pressure and in particular low residence times of less than 1 sec (see e.g. plasma torch in US 2009/0130442 above) or low power/low pressure with unspecified residence time (see e.g. glow discharge in a rotating drum reactor in WO 2012/076853 above).

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Therefore, the object of this invention is the provision of a new process modifying carbon particles. Preferably, this process shows a high flexibility according to the above mentioned parameters, such as power, residence time in the reactive zone (RZ) or starting material. Another object of the present invention is the provision of new products derived from this process.

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The object is achieved by a process for modifying carbon particles (CP1) within an apparatus (A1) which comprises a sample holder (SH) located below a reactive zone (RZ), wherein the process comprises the following steps a) to d):

15

- a) provision of carbon particles (CP1) on the sample holder (SH) of apparatus (A1),
- b) fluidizing the carbon particles (CP1) in apparatus (A1) with a gaseous stream (G1) into the reactive zone (RZ),
- c) keeping the carbon particles (CP1) with the gaseous stream (G1) in the reactive zone (RZ) for at least 1 sec, and feeding energy of at least 2,4 kJ into the reactive zone (RZ), and
- d) modification of the carbon particles (CP1) in the reactive zone (RZ) to obtain modified carbon particles (CP2).

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Surprisingly, these process features allowed various modifications, including expansion, surface modifications, morphological modifications, surface exfoliation, grafting of functional groups and different degrees of modification without changing the setup of the process.

Another major advantage is that in this process a high flexibility according to treatment time, treatment energy, possible process gases, number of possible process steps, variety of particles that can be treated and/or source of excitation energy is obtained.

30

Another advantage is that any kind of gas or gas mixture, e.g. inert, reactive, corrosive or toxic gases or any kind of compound with suitable vapor pressures can be used in a controlled way, such as Ar, He, H₂, N₂, CO₂, CH₄, CH₂Cl₂, Cl₂, NH₃, BCl₃, BF₃, HCl, a gas that generates O-, N-, S-, P- Si-, H-, C- or halogen containing functional groups on the carbon particles (CP1) surface, a gas that introduces B or N atoms in the carbon particles (CP1) or a mixture of any gas thereof. The at least one gas is preferably selected from Ar, H₂, N₂, CO₂ and/or NH₃, the at least one gas is more preferably selected from Ar, H₂ and/or N₂.

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Another major advantage is the high flexibility according to the process excitation power and treatment/reaction times at variable pressure.

5 Another advantage is that when a low pressure is used, a stable plasma can be maintained using the mentioned different plasma gas mixtures. This is possible even at relatively low excitation energies.

10 Another advantage is that stable plasma can be maintained using the mentioned different plasma gas mixtures at variable pressure, i.e. at low or at high pressure.

Another advantage is that more than one step can be performed in the process, wherein each step can be different, e.g. treatment with H₂ plasma in the first step and treatment with N₂ plasma in the second step.

15 Another advantage is the incorporation of nitrogen into carbon particles (CP1) with varying the content of nitrogen being incorporated.

20 Another advantage if graphites are used is that the layer rims and edges are modified in the process and/or expansion and/or delamination of the particles can be obtained.

Another advantage if graphites are used is that some of the bulk characteristics of the carbon particles (CP1) comprising bulk elemental composition, (graphene) layer distance and/or specific surface area can be retained after the modification.

25 Another advantage if graphites are used is that the modified graphites show exfoliation properties, which can be used for graphene nanoplatelet or nanoscale graphite synthesis.

30 Another advantage is that the interaction of the treated graphene nanoplatelets with gases or liquids is enhanced, e.g. dispersions of the treated graphene nanoplatelets can be obtained.

35 Another advantage is that carbon blacks can be strongly surface and bulk modified with functional groups and/or heteroatom incorporation. Furthermore, these modified materials exhibit a high surface area as well as good conductivities.

Surprisingly, in one embodiment of the present invention, if carbon black is used, the modified carbon black shows better dispersability in composite/hybrid materials.

40 Surprisingly, in one embodiment of the present invention, it is possible to expand graphite without having a step of intercalation.

The process according to the invention for modifying carbon particles (CP1) within an apparatus (A1) is defined in detail hereinafter.

Apparatus (A1) usually comprises at least one inlet for gaseous stream (G1), a reactive zone (RZ), a sample holder (SH) located below the reactive zone (RZ) and an outlet (O1) located at the top of (A1).

All parts and components of apparatus (A1) are known to the person skilled in the art.

Within the context of the present invention, the reactive zone (RZ) is the area inside apparatus (A1) in which reactions of carbon particles (CP1) take place. This area can consume a large area inside apparatus (A1).

Furthermore, the sample holder in apparatus (A1) is freely adjustable to the conditions needed and can be a glass frit or anything which is suitable by any means known to a person skilled in the art. The sample holder (SH) may serve for the gas distribution of gaseous stream (G1), to make sure that gaseous stream (G1) is being equalized and to provide a homogeneous fluidization of the carbon particles (CP1). Further the sample holder (SH) may serve for the carbon particles (CP1) to not fall into the gas supply line.

Carbon particles (CP1) according to the present invention are different forms of carbon, comprising natural graphite, synthetic graphite, expandable graphite, intercalated graphite, graphite, graphite oxide, expanded graphite, carbon black, activated carbon, carbon fibers, carbon nanotubes, fullerenes, graphene, graphene nanoplatelets, coal, coke and/or other forms of carbon, wherein any mixtures and composites of the aforementioned materials are possible and wherein these carbon particles (CP1) can be used in various forms and shapes including but not limited to expandable and/or intercalated materials, spherical particles, fibers or platelets .

Within the context of the present invention, intercalated graphite is obtained from graphite after an intercalation step, and can be e.g. a graphite sulfate or graphite nitrate based intercalation compound of different degrees of intercalation, or a graphite containing other intercalants, resulting in compounds with variable stoichiometry. This intercalated graphite is then expandable.

Within the context of the present invention, "modification" is defined as follows: morphological modification, which can manifest in the alteration of the dimensions, aspect ratio, shape, optical appearance, or form of phase domains in substances (e.g. expansion of layered materials) and which is mainly seen as resulting in structural changes of the carbon particles (CP1) without substantially altering the chemical constitution.

Chemical modification (functionalization) is the altering of at least one feature of the chemical constitution of a material which includes an exchange or introduction of functional groups (e.g. O-, N-, S-, P-, Si-, H-, C-containing groups) and/or functional coatings to a material or introduction of heteroatoms (e.g. O, C, S, B or N) on the surface or into the atomic structure of the materials.

Within the context of the present invention, "graphene" is understood to mean a monolayer of carbon atoms arranged in a two-dimensional honeycomb network.

"Graphene nanoplatelets" in the terms of the present invention are however not restricted to a material consisting exclusively of single-layer graphene (i.e. graphene in the proper sense and according to the IUPAC definition), but, like in many publications and as used by most commercial providers, rather denotes a bulk material, which is generally a mixture of a single-layer material, a bi-layer material and a material containing 3 to 10 layers and sometimes even more than 20 layers. The ratio of the different materials (single, two and multiple layers) depends on the production process. By way of example, suitable graphene materials and methods for preparing them are, for example, described in Macromolecules 2010, 43, pages 6515 to 6530, in WO 2009/126592, J. Phys. Chem. B 2006, 110, 8535-8539, Chem. Mater. 2007, 19, 4396-4404 or in the literature cited therein.

Within the context of the present invention, "graphite" is understood to be composed of stacked graphene sheets of linked hexagonal rings. In contrast to graphene, graphite in terms of the present invention is characterized by an essentially higher content of 20 and more layers than graphene.

In the context of the present invention, graphite is further understood to mean all types of graphite including crystalline flake graphite, amorphous graphite, lump graphite, graphite fiber, expanded graphite, intercalated graphite, expandable graphite, synthetic graphite, and natural graphite.

Further, in the context of the present invention, natural graphite is understood to be graphite which is not intercalated.

Within the context of the present invention, "fullerenes" are allotropes of carbon in the form of a hollow sphere, ellipsoid or tube. Spherical fullerenes are also called buckyballs; cylindrical ones are called carbon nanotubes or buckytubes.

Within the context of the present invention, "carbon nanotubes" (CNTs) are allotropes of carbon with a cylindrical nanostructure and are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the

nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, π -stacking. It is preferable that the diameter of the individual tubes is from 4 to 20 nm, in particular from 5 to 10 nm. The exterior shape of the tubes can moreover vary and can have uniform internal and external diameter, but it is also possible to produce tubes in the shape of a knot and to produce vermicular structures. The aspect ratio (length of respective graphite tube in relation to its diameter) is at least 10, preferably at least 5. The length of the nanotubes is at least 10 nm.

CNTs, and also the synthesis thereof, are described, for example, in J. Hu et al., Acc. Chem. Res. 32 (1999), 435-445. Suitable CNTs are described, for example, in DE-A-102 43 592, EP-A-2 049 597, DE-A-102 59 498, WO 2006/026691 and WO 2009/000408.

Within the context of the present invention, "carbon black" is a form of amorphous carbon that has a high surface-area-to-volume ratio. It is produced by the incomplete combustion of hydrocarbon and petroleum precursors such as coal tar, ethylene cracking tar, fluid catalytic cracking (FCC) tar and a small amount from vegetable oil. Carbon black is preferably a conductive carbon black. Suitable carbon blacks are for example described in D. Pantea et al., Applied Surface Science 2003, 217, 181-193.

Within the context of the present invention, the gaseous stream (G1) can have up to 50000 sccm, preferably up to 2000 sccm, more preferably up to 500 sccm. In principle, there is no upper limit for the gas flow.

Within the context of the present invention, in step a), carbon particles (CP1) as defined above are provided on the sample holder (SH) of apparatus (A1).

Within the context of the present invention, in step b), carbon particles (CP1) as defined above are fluidized in apparatus (A1) with a gaseous stream (G1) into the reactive zone (RZ). Here, the expression "fluidizing with a gaseous stream" is understood to mean a continuous flow of inert and/or reactive gas through the sample holder and the reactive zone (RZ). Hereby the increase of the velocity of gaseous stream (G1) is preferably above the minimal fluidization velocity of the carbon particles (CP1) and the loosening point of the packed bed, respectively, but below the sinking velocity of the carbon particles (CP1), so that the carbon particles (CP1) are not forwarded out of the reactive zone (RZ). Therefore, the settling velocity of the carbon particles (CP1) preferably is equal to the velocity of the upflowing gas stream (G1).

Within the context of the present invention, inert gases can contain, but are not limited to, Ar and He.

Within the context of the present invention, reactive gases can contain, but are not limited to, gases that generate O-, N-, S-, P- Si-, H-, C- or halogen containing functional groups on the material surface, a gas that introduces B or N atoms in the materials atomic structure or a mixture thereof, preferably H₂, N₂ or CO₂.

Within the context of the present invention, gaseous stream (G1) contains at least one gas selected from Ar, He, H₂, N₂, CO₂, CH₄, CH₂Cl₂, Cl₂, NH₃, BCl₃, BF₃, HCl, a gas that generates O-, N-, S-, P- Si-, H-, C- or halogen containing functional groups on the surface of carbon particles (CP1), a gas that introduces B or N atoms in the carbon particles (CP1) or a mixture of any gas thereof. The at least one gas is preferably selected from Ar, H₂, N₂, CO₂ and/or NH₃, the at least one gas is more preferably selected from Ar, H₂ and/or N₂.

Within the context of the present invention, in step c), the carbon particles (CP1) are kept with the gaseous stream (G1) in the reactive zone (RZ) for at least for 1 sec, and an energy of at least 2,4 kJ is fed into the reactive zone (RZ). Step c) is preferably carried out as a plasma activation step.

It is preferred that the power fed into the reactive zone (RZ) is between 0,1 and 5 kW, preferably between 0,2 and 3 kW, and most preferably between 0,7 and 1,6 kW, wherein the energy value is not below 2,4 kJ.

It is also preferred that the time of the carbon particles (CP1) kept in the reactive zone (RZ) is between 1 second and 7 days, preferably between 1 second and 2 days, more preferably between 1 second and 12 hours, and most preferably between 1 second and 1 hour, wherein the energy value is not below 2,4 kJ.

In a more preferable embodiment of the present invention, the time of the carbon particles (CP1) kept in the reactive zone (RZ) is between 10 second and 7 days, preferably between more than 10 second and 2 days, more preferably between 10 second and 12 hours and most preferably between 10 second and 1 hour, wherein the energy value is not below 2,4 kJ.

In a even more preferable embodiment of the present invention, the time of the carbon particles (CP1) kept in the reactive zone (RZ) is between 20 second and 7 days, preferably between more than 20 second and 2 days, more preferably between 20 second and 12 hours and most preferably between 20 second and 1 hour, wherein the energy value is not below 2,4 kJ.

In a most preferable embodiment of the present invention, the time of the carbon particles (CP1) kept in the reactive zone (RZ) is between 60 second and 7 days, preferably between more than 60 second and 2 days, more preferably between 60

second and 12 hours and most preferably between 60 second and 1 hour, wherein the energy value is not below 2,4 kJ.

In order to achieve high residence times of the particles (CP1) in the reactive zone (RZ), the gas flow of the gaseous stream (G1) may be fine tuned to the specific particles to be treated.

In one embodiment of the invention, the value of the energy fed into the reactive zone (RZ) in step c) is not below 30 kJ, preferably not below 60 kJ.

Within the context of the present invention, in step d), modification of carbon particles (CP1) is carried out in the reactive zone (RZ) in order to obtain modified carbon particles (CP2). The modification takes place in the reactive zone (RZ), due to the conditions as provided in step c). Therefore, it is important to keep the carbon particles (CP1) long enough (for at least 1 sec) in this reactive zone (RZ) to achieve better and more complete results. Here, more than one step of modification and different kinds of modification (morphological and chemical, as defined above) are possible, which can be seen for instance in examples 1 and 2. It is also possible to have consecutive expansion and chemical modification, for example the introduction of heteroatoms, like N, O, C, S or B.

Within the context of the present invention, the modification according to step d) can comprise expansion, surface modification, morphological modification, chemical modification (e.g. grafting of functional groups), surface exfoliation, and/or different degrees of modification.

It is preferred within the process of the present invention that the carbon particles (CP1) are modified according to step d) by plasma activation in step c), preferably by radio frequency plasma activation. In particular, the process according to the present invention in particular (according to steps b) to d)) is carried out as a fluidized bed plasma process, in particular by a fluidized bed plasma process with radio frequency plasma activation.

In one embodiment of the invention, more than one modification step d) can be performed without removing the carbon particles (CP1) to be treated from apparatus (A1), which can result in carbon particles (CP2) with at least two different modifications.

In one embodiment of the invention, the carbon particles (CP1) are fluidized in step b), subsequently employing at least two different gaseous streams (G1) in order to subsequently carry out the at least two different modification steps d).

In one embodiment of the invention, in step d), morphological modification and chemical modification take place simultaneously, or morphological modification and chemical modification are temporally separated.

In one embodiment of the invention, in step d), synthetic graphite is expanded in a single modification step.

- 5 In one embodiment of the invention, in step d), synthetic graphite is surface expanded in a single modification step.

In one embodiment of the invention, the system pressure can be kept between 50 mbar and 0.05 mbar, preferably between 25 and 0.05 mbar, preferably between 10 and 0.05
10 mbar, most preferably between 1 and 0.05 mbar.

Another subject of the present invention are modified carbon particles (CP2) as such. These modified carbon particles (CP2) can be produced according to the process as described above.

15

In one embodiment of the invention, in these carbon particles (CP2), layer rims and/or edges are modified and/or the carbon particles are expanded and/or delaminated in relation to carbon particles (CP1).

- 20 In one embodiment of the invention, modified carbon particles (CP2) are produced, wherein

- i) in case graphites or graphene nanoplatelets are employed as carbon particles (CP1), the characteristics comprising elemental composition, layer distance
25 and/or specific surface area are retained after the modification according to step d), or
- ii) in case carbon black is employed as carbon particles (CP1), the characteristics comprising morphology, average pore size, electrical conductivity, and/or specific surface area are retained after the modification according to step d).

30

A preferred embodiment of the invention may comprise a process for modifying carbon particles (CP1) by a fluidized bed plasma process within an apparatus (A1) which comprises a sample holder (SH) located below a reactive zone (RZ), wherein the process comprises the following steps a) to d):

35

- a) provision of carbon particles (CP1) on the sample holder (SH) of apparatus (A1),
- b) fluidizing the carbon particles (CP1) in apparatus (A1) with a gaseous stream (G1) into the reactive zone (RZ),
- 40 c) keeping the carbon particles (CP1) with the gaseous stream (G1) in the reactive zone (RZ) for at least 1 sec and feeding energy of at least 2,4 kJ into the reactive zone (RZ), and
- d) modification of the carbon particles (CP1) in the reactive zone (RZ) to obtain

modified carbon particles (CP2).

Examples:

5 General experimental procedure

The hereby disclosed process is designed as a fluidized bed plasma process with standard access to various gases to the reactor (apparatus (A1)).

10 All carbon particles are dried at 120°C in vacuum for at least 12 h prior to loading them into the reactor. After filling in the particles, the reactor is evacuated. The generator is then switched on, and the plasma is ignited without any gas flow at low pressure ($P < 0.1$ mbar). Then the gas flow is increased to the process flow rate. This also starts the fluidization of the particles. For the performed experiments, the operating pressure
15 during plasma modifications is about 0.2 – 2 mbar. Typical gas flow rates are in the range of 20 – 500 sccm. The experiments were carried out for 30 minutes under stable plasma conditions. After synthesis, the product is collected.

HP stands for high power (e.g. 1,5 kW), LP stands for low power (e.g. 0,75 kW).

20

X-ray photoelectron spectroscopy (XPS) is used to study the energy levels of atomic core electrons, primarily in solids and is applied here as analysis tool.

25

For determination of particle size distribution of a granular material, the unit [mesh] is often used.

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The Brunauer–Emmett–Teller (BET) theory explains the physical adsorption of gas molecules on a solid surface. Therefore, it is the basis for an analysis technique for the measurement of the specific surface area of a material. However, here the BET area is measured for carbon black in m²/g.

Example 1 (Graphites)

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Two different graphite grades were chosen as examples. Table 1 (below) lists the particle size, the typical reactor loading and amount of recovered product, as well as the plasma treatments carried out marked with X.

12

Material	Graphite powder (-20 +84 mesh)	Graphite flakes (-10 mesh)
Particle size	841 - 177 μm	< 2 mm lateral size
Reactor loading (g)	40	20
Recovered product (g)	> 30	> 10
Performed plasma treatments		
Ar	X	X
He	X	X
H ₂	X	X
N ₂	X	X
Ar/CO ₂	X	X
Ar/NH ₃	X	X
Ar/H ₂ /N ₂	X	X
Ar/CO ₂ /H ₂		X
CO ₂ /N ₂		X
CO ₂ /N ₂ /H ₂		X

Table 2 (below) shows elemental composition of the particle surface of plasma treated graphite powder (graphite powder -20 +84 mesh) based on XPS analysis.

Experiment	C at%	O at%	N at%
untreated	97,9	1,9	0,0
Ar-plasma 1 kW	97,2	2,7	0,0
H ₂ -plasma 2,47 kW	96,6	2,9	0,0
Ar/CO ₂ -plasma 2,5 kW	95,6	4,1	0,0
N ₂ -plasma HP 1,5 kW	85,3	3,1	11,5
N ₂ -plasma LP 0,75 kW	93,2	2,7	3,3
Ar/NH ₃ -plasma 3 kW	96,0	2,6	1,2
H ₂ /N ₂ -plasma Ratio 3.6 : 1, 2 kW	93,6	3,7	1,8

Table 3 (below) shows elemental composition of the particle surface of plasma treated graphite flakes (graphite flakes -10 mesh) based on XPS analysis.

Experiment	C at%	O at%	N at%
untreated	99,0	0,9	0,0
Ar plasma 1,5 kW	98,2	1,5	0,0
Ar/H ₂ plasma 3,3 kW	98,3	1,6	0,0
Ar/CO ₂ plasma 2 kW	95,8	3,6	0,3

N ₂ plasma HP 1,7 kW	87,6	2,9	9,3
N ₂ plasma LP 0,8 kW	95,3	1,8	2,9
Ar/NH ₃ plasma 2,5 kW	97,7	1,9	0,2
Ar/H ₂ /N ₂ plasma 2 kW	97,1	2,3	0,4
Ar/H ₂ /CO ₂ plasma 3,3 kW	97,9	2,0	0,0
CO ₂ /N ₂ plasma 3,8 kW	95,8	2,8	0,6
CO ₂ /N ₂ /H ₂ -plasma 4 kW	97,9	2,1	0,0

Conclusion:

Graphite powder (-20 +84 mesh) was successfully modified in various plasma atmospheres and functional groups were grafted onto the particles surface. XPS analysis confirms an increase of the oxygen and/or nitrogen content at the material surface after respective treatments. Further, surface morphology significantly changes and all plasma treatments lead to expansion of graphite layers. Since also Ar and H₂ treated material shows this effect, it seems to be a general plasma related effect and not dependent on the specific chemistry of the process gas mixtures used. Furthermore, especially N₂ and NH₃ plasma treatments lead to chemical attack, resulting in morphology changes of the particles surface.

Graphite flakes (-10 mesh) show in general the same trends for modified graphite flake material, although a somewhat lower tendency for surface expansion of graphite layers is observed by SEM probably due to the intrinsically superior graphitic structure of the graphite flakes compared to the graphite powder.

Example 2 (Carbon black)

Table 4 (below) lists the BET area of the pristine particles, the typical reactor loading and amount of recovered product as well as the plasma treatments carried out marked with X.

Material	Vulcan XC72	CB1	Printex XE2
BET area (m ² /g)	206.3	73.5	1056.1
Reactor loading (g)	5	4	3
Recovered product (g)	3.5 - 4	3	2.5
Performed plasma treatments			
Ar	X	X	X
Ar/H ₂	X	X	X
Ar/CO ₂	X	X	X
Ar/N ₂	X	X	X
NH ₃	X	X	X
H ₂ /N ₂	X	X	X

Remarks to the experimental procedure: the commercial carbon black particles Vulcan XC72 and Printex XE2 were homogenized by ball milling prior to loading them in the reactor.

Table 5 (below) lists bulk elemental composition of Vulcan XC72, CB1 and Printex XE2 samples after treatment in the various plasma atmospheres. The detection limit of the elements C, O, N and H is approximately 0.5 wt%. Therefore given values of < 0.5 wt% indicate no detection of the respective element. The sensitivity of Printex XE2 powder is lower than usual resulting in a detection limit of 1 wt%.

Experiment	C wt%	O wt%	N wt%	H wt%	S wt%
Vulcan XC72	98,9	< 0.5	< 0.5	< 0.5	0.58
Ar plasma (0.3 kW)	99	< 0.5	< 0.5	< 0.5	0.62
Ar/H ₂ plasma (0.5 kW)	98.4	0.6	< 0.5	< 0.5	0.59
Ar/CO ₂ plasma (0.4 kW)	97	1,3	< 0.5	< 0.5	0.62
Ar/N ₂ plasma LP (0.35 kW)	99	0,9	0,6	< 0.5	0.58
N ₂ plasma HP (1.5kW)	95	0,6	2,8	< 0.5	0.56
NH ₃ plasma (0.4kW)	97	0.5	1,8	< 0.5	0.58
H ₂ /N ₂ plasma (0.5kW)	99	< 0.5	< 0.5	< 0.5	0.6

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CB1	99,6	< 0.5	< 0.5	< 0.5	< 0.01
Ar plasma (0.3 kW)	not measured				
Ar/H ₂ plasma (0.5 kW)	99.7	< 0.5	< 0.5	< 0.5	< 0.01
Ar/CO ₂ plasma (0.4 kW)	99,8	< 0.5	< 0.5	< 0.5	< 0.01
Ar/N ₂ plasma HP (1.5kW)	98,8	< 0.5	0.5	< 0.5	< 0.01
Ar/N ₂ plasma LP (0.4 kW)	97	0.8	2.6	< 0.5	< 0.01
NH ₃ plasma (0.4 kW)	99,5	0.6	< 0.5	< 0.5	< 0.01
H ₂ /N ₂ plasma (0.5 kW)	98,6	0.9	< 0.5	< 0.5	< 0.01
Printex XE2	98.2	< 1	< 0.5	< 0.5	0.12
Ar plasma (0.3 kW)	98	ca. 2	< 1	< 1	0,09
Ar/H ₂ plasma (0.5 kW)	98.6	0.9	< 0.5	< 0.5	0.12
Ar/CO ₂ plasma (0.4 kW)	96	ca. 1	ca. 2	< 1	0,08
Ar/N ₂ plasma HP (1.5kW)	95	ca. 1	ca. 3	< 1	0,1
Ar/N ₂ plasma LP (0.4 kW)	97	0.5	2.4	< 0.5	0.11
NH ₃ plasma (0.4 kW)	97	ca. 1	< 1	< 1	0,09
H ₂ /N ₂ plasma (0.5 kW)	98	ca. 1	< 1	< 1	0,1

Table 6 (below) shows elemental composition of the material surface of plasma treated Vulcan XC72 based on XPS data.

Experiment Vulcan XC72	C at%	O at%	N at%
untreated	97,7	2,2	0
Ar plasma 0,3 kW	93,9	5,8	0,0
Ar/H ₂ plasma 0,5 kW	94,3	5,3	0,0
Ar/CO ₂ plasma 0,4 kW	90,3	9,6	0,0
Ar/N ₂ plasma LP 0,35 kW	92,4	6,9	0,6
N ₂ plasma HP 1,5 kW	93,1	4,9	1,9

NH ₃ plasma 0,4 kW	91,5	5,9	2,2
H ₂ /N ₂ plasma 0,5 kW	93,8	5,8	0,2

Table 7 (below) shows elemental composition of the material surface of plasma treated CB1 based on XPS data.

Experiment	C at%	O at%	N at%
CB1			
untreated	97,2	2,7	0,0
Ar plasma 0,3 kW	97,4	2,6	0,0
Ar/H ₂ plasma 0,5 kW	95,9	4,0	0,0
Ar/CO ₂ plasma 0,4 kW	95,2	4,5	0,2
Ar/N ₂ plasma LP 0,35 kW	96,0	2,4	1,5
Ar/N ₂ plasma HP 1,5 kW	94,3	4,4	0,9
NH ₃ plasma 0,4 kW	94,4	4,4	0,9
H ₂ /N ₂ plasma 0,5 kW	93,0	6,9	0,0

Table 8 (below) shows elemental composition of the material surface of plasma treated Printex XE2 based on XPS data.

Experiment Printex XE2	C at%	O at%	N at%
untreated	96,3	3,7	0,0
Ar plasma 0,3 kW	92,7	7,3	0,0
Ar/H ₂ plasma 0,5 kW	90,8	9,2	0,0
Ar/CO ₂ plasma 0,4 kW	91,8	6,8	1,3
Ar/N ₂ plasma LP 0,35 kW	93,8	4,3	1,7
Ar/N ₂ plasma HP 1,5 kW	93,8	4,3	1,7
NH ₃ plasma 0,4 kW	92,9	7,0	0,0
H ₂ /N ₂ plasma 0,5 kW	95,5	3,4	1,1

Conclusion:

- 5 Carbon black with different surface area (CB1: 76 m₂/g, Vulcan XC72: 206 m₂/g, Printex XE2: 1056 m₂/g) were successfully modified by plasma treatment with various gas mixtures (nitrogen and oxygen containing).

Elemental analysis indicates modification with nitrogen for all treated materials.
 10 Furthermore a higher nitrogen content (> 2 wt%) is observed for samples treated at high generator power (1.5 kW) compared to the nitrogen content of samples treated at low generator power. CO₂ modification is also confirmed for Vulcan samples by elemental analysis. Analysis of XPS data confirms the incorporation of nitrogen as well as oxygen containing groups in the modified materials. As in the case of graphite
 15 modification N₂ plasma appears to be the most effective in terms of nitrogen doping.

Claims

1. A process for modifying carbon particles (CP1) within an apparatus (A1) which
5 comprises a sample holder (SH) located below a reactive zone (RZ), wherein the process comprises the following steps a) to d):
 - a) provision of carbon particles (CP1) on the sample holder (SH) of apparatus (A1),
 - 10 b) fluidizing the carbon particles (CP1) in apparatus (A1) with a gaseous stream (G1) into the reactive zone (RZ),
 - c) keeping the carbon particles (CP1) with the gaseous stream (G1) in the reactive zone (RZ) for at least 1 sec and feeding energy of at least 2,4 kJ into the reactive zone (RZ), and
 - 15 d) modification of the carbon particles (CP1) in the reactive zone (RZ) to obtain modified carbon particles (CP2).
2. A process according to claim 1, wherein the carbon particles (CP1) are natural
20 graphite, synthetic graphite, expandable graphite, intercalated graphite, graphite, graphite oxide, expanded graphite, activated carbon, carbon fibers, carbon nanotubes, fullerenes, graphene, graphene nanoplatelets, coal, coke, carbon black, and/or other carbons.
3. A process according to any of claims 1 and 2, wherein gaseous stream (G1)
25 contains at least one gas selected from Ar, He, H₂, N₂, CO₂, CH₄, CH₂Cl₂, Cl₂, NH₃, BCl₃, BF₃, HCl, a gas that generates O-, N-, S-, P-, Si-, H-, C- or halogen containing functional groups on the surface of carbon particles (CP1), a gas that introduces B or N atoms in the carbon particles (CP1) or a mixture of any gas thereof, the at least one gas is preferably selected from Ar, H₂, N₂, CO₂ and/or
30 NH₃, the at least one gas is more preferably selected from Ar, H₂ and/or N₂.
4. A process according to any of claims 1 to 3, wherein the modification according
35 to step d) comprises expansion, surface modification, morphological modification, chemical modification, surface exfoliation, grafting of functional groups and/or different degrees of modification.
5. A process according to any of claims 1 to 4, wherein the power fed into the
40 reactive zone (RZ) is between 0,1 and 5 kW, preferably between 0,2 and 3 kW, and most preferably between 0,7 and 1,6 kW, wherein the energy value is not below 2,4 kJ.
6. A process according to any of claims 1 and 5, wherein the time of the carbon

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particles (CP1) kept in the reactive zone (RZ) is between 60 seconds and 7 days, preferably between 60 seconds and 2 days, more preferably between 60 seconds and 12 hours, and most preferably between 60 seconds and 1 hour, wherein the energy value is not below 2,4 kJ.

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7. A process according to any of claims 1 and 6, wherein more than one modification step d) can be performed without removing the carbon particles (CP1) to be treated from apparatus (A1) and which can result in carbon particles (CP2) with at least two different modifications.

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8. A process according to any of claims 1 and 7, wherein the carbon particles (CP1) are fluidized in step b), subsequently employing at least two different gaseous streams (G1) in order to subsequently carry out the at least two different modification steps d).

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9. A process according to any of claims 1 and 8, wherein in step d) morphological modification and chemical modification take place simultaneously or morphological modification and chemical modification are temporally separated.

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10. A process according to any of claims 1 and 9, wherein the modified carbon particles (CP2) comprise nitrogen.

11. A process according to any of claims 1 and 10, wherein in step d) synthetic graphite is expanded in a single modification step.

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12. A process according to any of claims 1 and 11, wherein the system pressure can be kept between 50 mbar and 0.05 mbar, preferably between 25 and 0.05 mbar, preferably between 10 and 0.05 mbar, most preferably between 1 and 0.05 mbar.

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13. Modified carbon particles (CP2), produced according to the process of any of claims 1 to 12.

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14. Modified carbon particles (CP2) according to claim 13, wherein layer rims and/or edges of the carbon particles are modified and/or wherein the carbon particles are expanded and/or delaminated in relation to carbon particles (CP1).

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15. Modified carbon particles (CP2) according to any of claims 13 and 14, wherein
- i) in case graphites or graphene nanoplatelets are employed as carbon particles (CP1), the characteristics comprising elemental composition, layer distance and/or specific surface area are retained after the modification according to step d), or

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- ii) in case carbon black is employed as carbon particles (CP1), the characteristics comprising morphology, average pore size, electrical conductivity and/or specific surface area are retained after the modification according to step d).

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16. A process for modifying carbon particles (CP1) according to any of claims 1 to 12 by a fluidized bed plasma process within an apparatus (A1) which comprises a sample holder (SH) located below a reactive zone (RZ), wherein the process comprises the following steps a) to d):

10

- a) provision of carbon particles (CP1) on the sample holder (SH) of apparatus (A1),
- b) fluidizing the carbon particles (CP1) in apparatus (A1) with a gaseous stream (G1) into the reactive zone (RZ),
- 15 c) keeping the carbon particles (CP1) with the gaseous stream (G1) in the reactive zone (RZ) for at least 1 sec and feeding energy of at least 2,4 kJ into the reactive zone (RZ), and
- d) modification of the carbon particles (CP1) in the reactive zone (RZ) to obtain modified carbon particles (CP2).

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/066411

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/02 C01B31/04 C09C1/56 B01J19/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B C09C B01J

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

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

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	M Heintze ET AL: "Surface functionalisation of carbon nano-fibres in fluidised bed plasma", Surface and Coatings Technology, 30 April 2003 (2003-04-30), pages 831-834, XP055187416, DOI: 10.1016/S0257-8972Z03.00410-9 Retrieved from the Internet: URL: http://www.sciencedirect.com/science/article/pii/S0257897203004109/pdf?md5=396f02fcd9ed149fbdf3fcf3a749056f&pid=1-s2.0-S0257897203004109-main.pdf [retrieved on 2015-05-05]	1-10, 12-14,16
A	the whole document ----- -/-	11,15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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09/10/2015

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/130442 A1 (CHRIST MARTIN [DE] ET AL) 21 May 2009 (2009-05-21) cited in the application examples	1-16
X	----- FELTEN A ET AL: "Radio-frequency plasma functionalization of carbon nanotubes surface O ₂ , NH ₃ , and CF ₄ treatments", JOURNAL OF APPLIED PHYSICS, AMERICAN INSTITUTE OF PHYSICS, US, vol. 98, no. 7, 7 October 2005 (2005-10-07), pages 74308-074308, XP012078724, ISSN: 0021-8979, DOI: 10.1063/1.2071455	1-14,16
A	"Abstract"; "Experiment"; "Overview of the experimental conditions"; tables	15
X	----- WO 2012/160041 A1 (NANOCYL SA [BE]; LUIZI FREDERIC [BE]; MINEA TIBERIU MARIAN [FR]; LUCAS) 29 November 2012 (2012-11-29)	1-14,16
A	paragraphs [0015], [0021]; examples; table 1 -----	15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/066411

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009130442 A1	21-05-2009	CN 101428792 A	13-05-2009
		DE 102007053652 A1	14-05-2009
		EP 2058278 A2	13-05-2009
		US 2009130442 A1	21-05-2009
		WO 2009060009 A2	14-05-2009

WO 2012160041 A1	29-11-2012	CN 103596878 A	19-02-2014
		EP 2714590 A1	09-04-2014
		ES 2539686 T3	03-07-2015
		JP 2014525820 A	02-10-2014
		KR 20140096994 A	06-08-2014
		US 2014248442 A1	04-09-2014
		WO 2012160041 A1	29-11-2012
