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Industry Canada

CA 2952148 A1 2016/01/21

(21) **2 952 148**

(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2015/07/15
(87) Date publication PCT/PCT Publication Date: 2016/01/21
(85) Entrée phase nationale/National Entry: 2016/12/13
(86) N° demande PCT/PCT Application No.: EP 2015/066212
(87) N° publication PCT/PCT Publication No.: 2016/008951
(30) Priorités/Priorities: 2014/07/15 (EP14177137.8);
2014/07/18 (EP14177643.5)

(51) Cl.Int./Int.Cl. *H01M 4/133*(2010.01),
C01B 32/00(2017.01), *C01B 32/21*(2017.01),
C01B 33/00(2006.01), *C09C 1/44*(2006.01),
H01M 4/1393(2010.01)

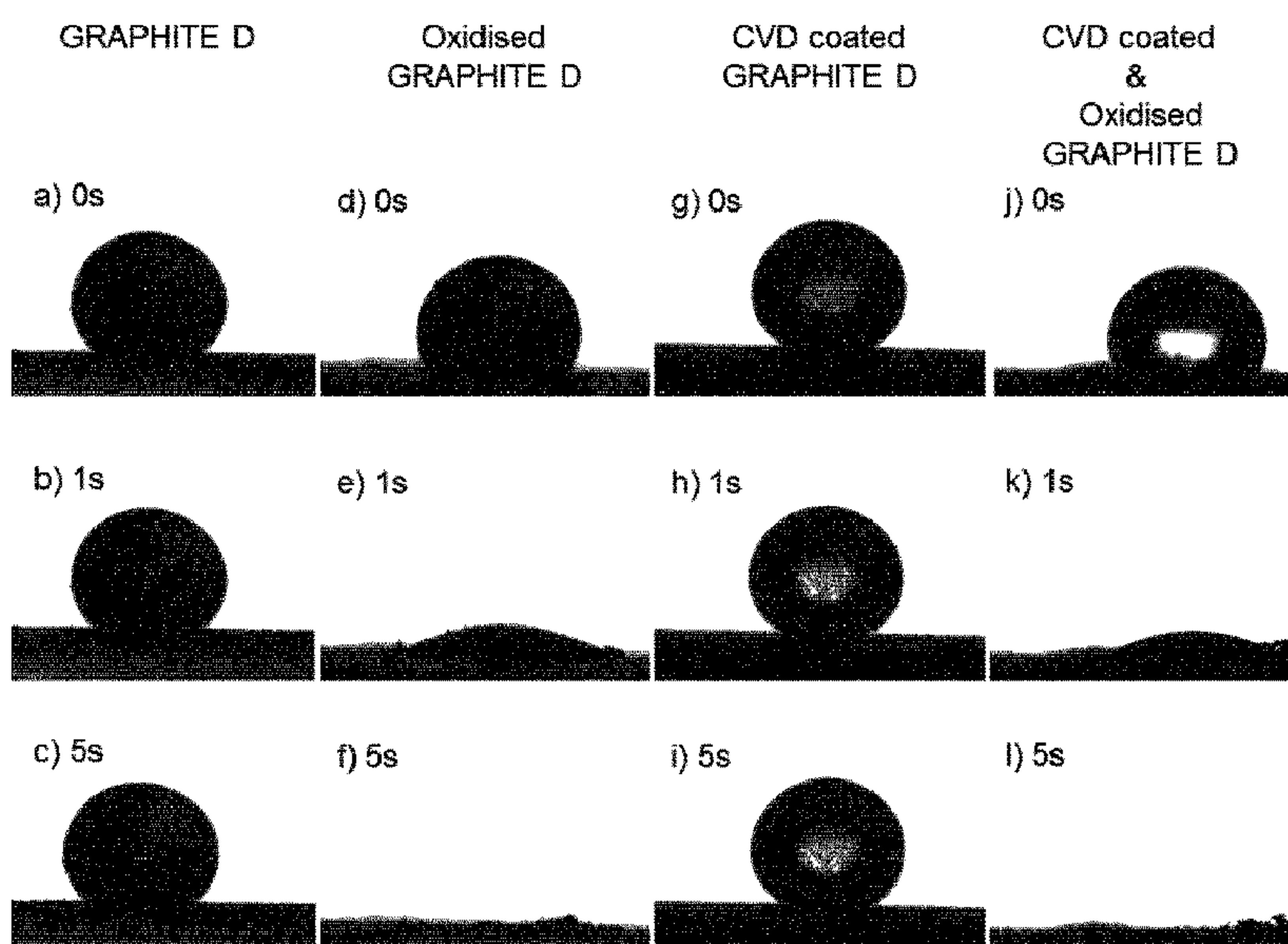
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(54) Titre : MATERIAU PARTICULAIRE CARBONE HYDROPHILE MODIFIÉ EN SURFACE
(54) Title: HYDROPHILIC SURFACE-MODIFIED CARBONACEOUS PARTICULATE MATERIAL

Figure 4: Wetting properties of starting material (GRAPHITE D) and treated material (CVD coated and oxidized GRAPHITE D) after 0s, 1s and 5s.



(57) Abrégé/Abstract:

The present disclosure relates to a novel surface-modified carbonaceous particulate material having a hydrophilic non-graphitic carbon coating. The material can for example be produced by CVD-coating of a carbonaceous particulate material such as

(57) Abrégé(suite)/Abstract(continued):

graphite followed by an oxidation treatment under defined conditions. The resulting material exhibits a more hydrophilic surface compared to an unmodified CVD-coated carbon material, which is desirable in many applications, such as when used as an active material in the negative electrode of lithium ion batteries or in a polymer composite material.

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

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2016/008951 A1

(43) International Publication Date
21 January 2016 (21.01.2016)

WIPO | PCT

(51) International Patent Classification:
C01B 31/02 (2006.01) H01M 4/587 (2010.01)
C01B 31/04 (2006.01)

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(21) International Application Number:
PCT/EP2015/066212

(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.

(22) International Filing Date:
15 July 2015 (15.07.2015)

(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).

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:
14177137.8 15 July 2014 (15.07.2014) EP
14177643.5 18 July 2014 (18.07.2014) EP

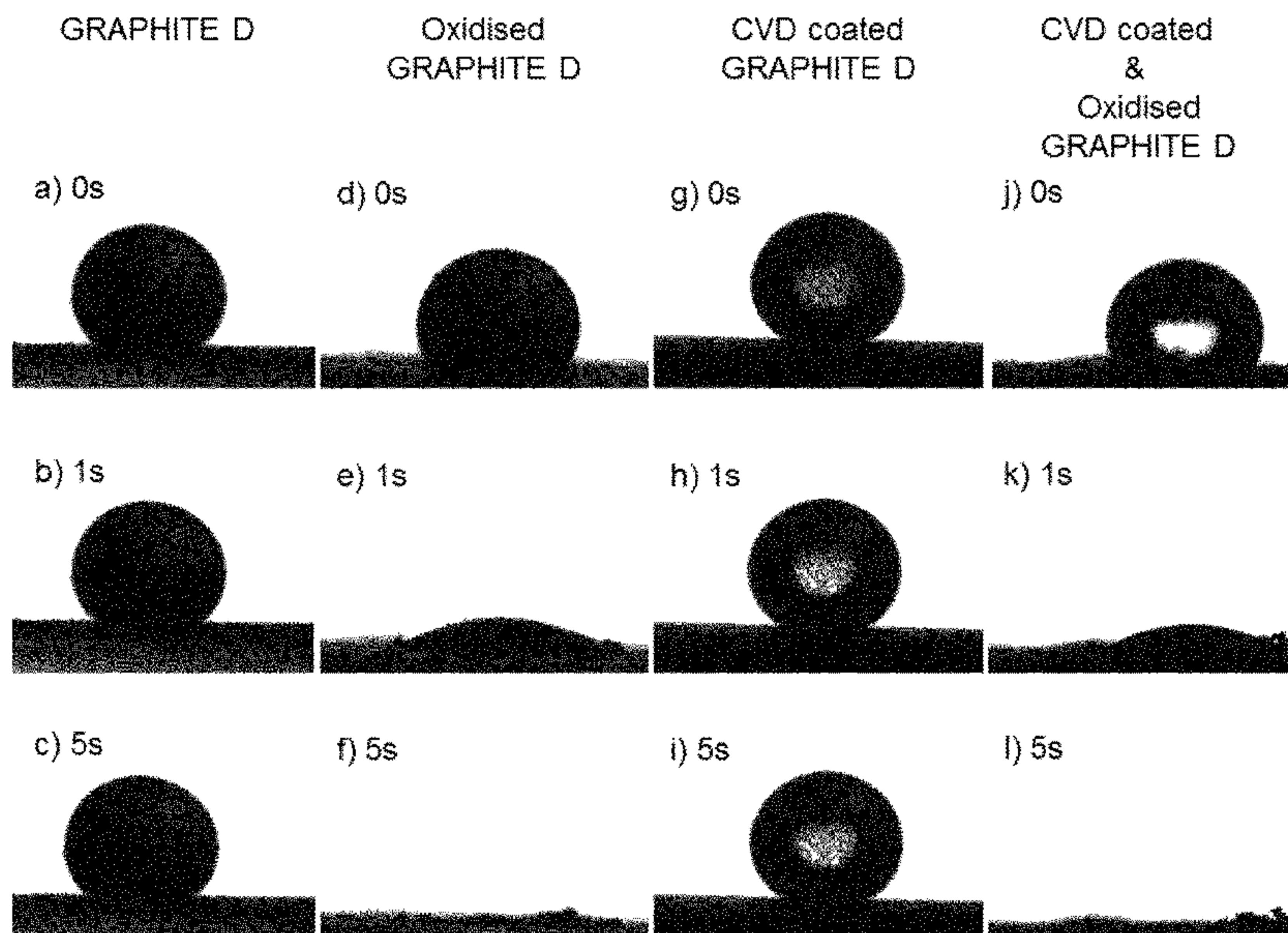
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[Continued on next page]

(54) Title: HYDROPHILIC SURFACE-MODIFIED CARBONACEOUS PARTICULATE MATERIAL

Figure 4: Wetting properties of starting material (GRAPHITE D) and treated material (CVD coated and oxidized GRAPHITE D) after 0s, 1s and 5s.



(57) **Abstract:** The present disclosure relates to a novel surface-modified carbonaceous particulate material having a hydrophilic non-graphitic carbon coating. The material can for example be produced by CVD-coating of a carbonaceous particulate material such as graphite followed by an oxidation treatment under defined conditions. The resulting material exhibits a more hydrophilic surface compared to an unmodified CVD-coated carbon material, which is desirable in many applications, such as when used as an active material in the negative electrode of lithium ion batteries or in a polymer composite material.

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WO 2016/008951 A1



Published:

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

Claims

1. A surface-modified carbonaceous particulate material comprising carbonaceous core particles with a hydrophilic non-graphitic carbon coating, wherein the hydrophilic surface-modified carbonaceous particulate material has a BET specific surface area (BET SSA) of below 49 m²/g, preferably less than 25 m²/g or less than 10 m²/g.
2. The hydrophilic surface-modified carbonaceous particulate material of claim 1, exhibiting a wettability characterized by
 - (i) a contact angle after 3 seconds that is less than 90°, preferably less than 75°, less than 70°, or less than 65°, and/or a contact angle after 5 seconds that is less than about 60°, preferably less than 40°, less than 30°, less than 25°, or less than 20°; and/or
 - (ii) a surface energy of said carbonaceous particulate material of at least 59 mJ/m², preferably at least 62, 67 or 70 mJ/m².
3. The surface-modified carbonaceous particulate material of claim 1 or claim 2, characterized by a spring-back ratio of about 15% to about 75%, preferably about 20 to 60% or 25 to 50 %.
4. The hydrophilic surface-modified carbonaceous particulate material of any one of claims 1 to 3, having a polycyclic aromatic hydrocarbon (PAH) concentration of less than 200 mg/kg, less than 150 mg/kg, less than 30 mg/kg, or less than 10 mg/kg.
5. The hydrophilic surface-modified carbonaceous particulate material of any one of claims 1 to 4, wherein the carbonaceous core particles are selected from natural graphite, synthetic graphite, coke, hard carbon, graphitized fine coke, mixtures thereof, or compositions of such carbon particles which further contain silicon, tin, bismuth, antimony, aluminum, silver, SiO_X (X = 0.2-1.8), or SnO₂ particles.
6. The hydrophilic surface-modified carbonaceous particulate material of any one of claims 1 to 5, wherein the carbonaceous core particles are synthetic graphite particles, or a mixture of synthetic graphite particles and silicon particles.
7. The hydrophilic surface-modified carbonaceous particulate material of any one of claims 1 to 6, wherein the carbon coating is comprised of oxidized amorphous carbon; preferably wherein the initial carbon coating before oxidation treatment is obtained by a chemical vapor (CVD) deposition process.
8. The hydrophilic surface-modified carbonaceous particulate material of any one of claims 1 to 7, characterized by
 - (i) an oxygen content of greater than about 200 ppm, greater than about 400

ppm, greater than about 600 ppm, greater than about 700 ppm, or greater than about 800 ppm; and/or

(ii) a BET surface area of from about 0.5 to about 5 m²/g, or from about 1.0 to about 5 m²/g, or from about 1.5 to about 4.1 m²/g; and/or

5 (iii) a mesopore area of less than 5.0 m²/g, less than 4 m²/g, less than 3.8 m²/g or less than 3.6 m²/g; and/or

(iv) a xylene density of from 2.1 to 2.260 g/cm³, preferably from 2.15 to 2.25 g/cm³; and/or

10 (v) an I_D/I_G ratio ($R(I_D/I_G)$) of larger than about 0.3, preferably by an $R(I_D/I_G)$ of between 0.4 and 1.0, when measured with a laser having an excitation wavelength of 632.8 nm.

9. A surface-modified carbonaceous particulate material comprising carbonaceous core particles with a hydrophilic non-graphitic carbon coating, wherein the hydrophilic surface-modified carbonaceous particulate material is characterized by a ratio between the BET SSA and the specific surface energy of less than 0.8, preferably less than 0.6, less than 0.5 less than 0.4, less than 0.3 or less than 0.2.

15 10. A surface-modified carbonaceous particulate material comprising carbonaceous core particles with a hydrophilic non-graphitic carbon coating, wherein the hydrophilic surface-modified carbonaceous particulate material is characterized by exhibiting a low viscosity in aqueous dispersion containing 40 weight% of said carbonaceous material, preferably wherein the viscosity of the dispersion containing 40 weight% of 20 said carbonaceous material is between 2,000 to 4,000 mPa·s.

25 11. A process for preparing a hydrophilic surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10, wherein carbonaceous particles are (a) coated with non-graphitic carbon, and (b) subjected to an oxidation treatment to increase the hydrophilicity of the coated carbonaceous particulate material obtained from step (a); preferably wherein the carbonaceous particles to be modified are selected from natural graphite, synthetic graphite, coke, hard carbon, mixtures thereof, or 30 compositions of such carbon particles which further contain silicon, tin, aluminum, silver, bismuth, antimony, SiO_X (X = 0.2-1.8), or SnO₂ particles.

35 12. The process of claim 11, wherein the non-graphitic carbon-coating of step a) is achieved by a method selected from chemical vapor deposition (CVD), physical vapor deposition (PVD), pitch-coating, pyrolysis, atomic layer deposition (ALD), laser ablation, sputtering, or evaporation.

13. The process of claim 11 or claim 12, wherein the chemical vapor deposition is carried out by contacting said carbonaceous particulate material with a hydrocarbon gas or alcohol vapor mixed with an inert carrier gas for a period ranging from 10 to 180 minutes; preferably wherein the hydrocarbon gas is an aliphatic or aromatic hydrocarbon selected from the group consisting of methane, ethane, ethylene, propane, propene, acetylene, butane, benzene, toluene, xylene, and combinations thereof, or wherein the alcohol is selected from the group consisting of ethanol, propanol, isopropanol, and combinations thereof.
5
14. The process of any one of claims 11 to 13, wherein the chemical vapor deposition is carried out at temperatures ranging from 500 to 1200 °C, or from 600 to 1100 °C, or from 700 to 1050 °C; and/or
wherein the hydrocarbon gas is acetylene or propane, the carrier gas is nitrogen; and/or
wherein the contacting period ranges from 10 to 180 minutes, from 10 to 120 minutes, 15 from 10 to 60 minutes, or from 20 to 40 minutes.
15. The process of any one of claims 11 to 14, wherein the oxidation treatment step b) is performed by contacting the carbonaceous particulate material obtained from step a) with an oxidant either in a gaseous / solid phase process with air, carbon dioxide, water vapor, oxygen, ozone, or any combination thereof, or, alternatively, in a liquid / solid phase process with aqueous hydrogen peroxide or other oxidants present in said liquid phase;
20 preferably
wherein the flow rate of the oxidant ranges from 1 to 50 l/min, or from 1 to 20 l/min, or from 2 to 5 l/min; and/or
wherein the oxidation treatment is performed at temperatures ranging from 500 to 25 900 °C, from 550 to 750 °C, or from 550 to 600 °C, with the proviso that when step b) is carried out with ozone, the oxidation treatment is performed at ambient temperature; and/or
wherein the oxidation treatment is performed for the period of 10 to 30 minutes, or 10 30 to 25 minutes, or 15 to 20 minutes.
16. The process of any one of claims 11 to 15, wherein
 - a) the BET SSA of the surface-modified carbonaceous particulate material obtained after step (b) is
 - (i) less than the BET SSA of the starting carbonaceous particulate material, 35 preferably wherein the BET SSA is reduced by between 10 and 90% compared to the starting material; and/or

(ii) equal to or greater than the BET SSA of the non-graphitic carbon-coated carbonaceous particulate material obtained from step (a); and/or

5 b) the D_{90} particle size distribution of the surface-modified carbonaceous particulate material obtained from step (b) is similar to

(i) the D_{90} particle size distribution of the non-graphitic carbon-coated carbonaceous particulate material obtained from step (a); and/or

(ii) the D_{90} particle size distribution of the starting carbonaceous particulate material,

10 preferably wherein the D_{90} particle size distribution value is within $\pm 10\%$, or within $\pm 5\%$ of the D_{90} particle size distribution value of the starting material; and/or

c) the mesopore area of the surface-modified carbonaceous particulate material obtained after step (b) is

(i) less than the mesopore area of the starting carbonaceous particulate material; and/or

15 (ii) equal to or greater than the mesopore area of the non-graphitic carbon-coated carbonaceous particulate material obtained from step (a); and/or

d) the xylene density of the hydrophilic surface-modified carbonaceous particulate material obtained from step (b) is reduced by between 1 and 7 %

20 compared to the xylene density of the starting carbonaceous particulate material.

17. The process of any one of claims 11 to 16, wherein

(i) the process steps (a) and (b) are carried out in the same reactor, preferably wherein the reactor is purged with inert gas after the non-graphitic carbon coating of step (a), and prior to the oxidative treatment of step (b); or

25 (ii) wherein the non-graphitic carbon-coated carbonaceous particulate material is recovered from the reactor, and is subsequently transferred into the same or a different reactor for the oxidative treatment of step (b).

18. A hydrophilic surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10, obtainable by a process of any one of claims 11 to 17.

30 19. A composition comprising the surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18.

20. The composition of claim 19, mixed together with one or more surface-modified carbonaceous particulate materials as defined in any one of claims 1 to 10 or 18, wherein the one or more additional surface-modified carbonaceous particulate

materials are different from the first surface-modified carbonaceous particulate material.

21. The composition of claim 19 or claim 20, in a mixture together with
 - (i) other unmodified or modified carbonaceous particulate material; 5 preferably wherein said additional carbonaceous particulate material is selected from the group consisting of natural or synthetic graphite, exfoliated graphite, carbon black, coke, graphene, graphene fibers, nanotubes, including carbon nanotubes, where the nanotubes are single-walled nanotubes (SWNT), multiwalled nanotubes (MWNT), or combinations of these; fullerenes, nanographite, graphitized fine coke, and 10 combinations thereof; or
 - (ii) in a mixture together with other non-carbonaceous materials in particulate form, or combinations thereof.
22. Use of the hydrophilic surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10, or 18 for preparing a negative electrode material for a 15 lithium ion battery.
23. A negative electrode of a lithium ion battery comprising the hydrophilic surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10, or 18 as an active material.
24. The negative electrode of a lithium ion battery of claim 23, wherein the carbonaceous 20 core particles comprises natural graphite and/or synthetic graphite and wherein the negative electrode further comprises additional natural graphite, synthetic graphite, and/or graphitized fine coke.
25. The negative electrode of claim 24, wherein the additional natural graphite and/or synthetic graphite is present in an amount ranging from 2% to 10%, or 3% to 5 % by 25 weight of the negative electrode.
26. The negative electrode of claim 24 or 25, wherein the average particle size of the additional natural graphite and/or synthetic graphite has an average particle size (D_{50}) ranging from 0.5 to 100 μm , or from 1 to 20 μm .
27. The negative electrode of any of claims 24-26, wherein the additional natural graphite, 30 synthetic graphite, and/or graphitized fine coke is pitch-coated.
28. A lithium ion battery comprising the hydrophilic surface-modified synthetic carbonaceous particulate material as defined in any one of claims 1 to 10, or 18 in the negative electrode of the battery.

29. The lithium ion battery of claim 28, wherein the irreversible charge loss in the 1st cycle determined in a lithium ion negative electrode half cell test is below 20% and/or wherein the irreversible charge loss in the 2nd cycle determined in a lithium ion negative electrode half cell test is less than 6%,
5 preferably wherein the improvement in the irreversible charge loss in the 1st cycle determined in a lithium ion negative electrode half cell test is at least about 10% compared to a control material without the oxidation treatment as defined in step b) of claim 11; and/or wherein the improvement in the irreversible charge loss in the 2nd cycle determined in
10 a lithium ion negative electrode half cell test is at least about 20% compared to a control material which has not undergone the oxidation treatment as defined in step b) of claim 11.

30. A polymer composite material comprising the hydrophilic surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10, or 18 in a
15 weight ratio of 5-95 % by weight, preferably 10-85 % by weight.

31. An energy storage device comprising the surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18.

32. A carbon brush comprising the surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18.

20 33. An electric vehicle, hybrid electric vehicle, or plug-in hybrid electric vehicle comprising a lithium ion battery, wherein said lithium ion battery comprises the surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18 as an active material in the negative electrode of the battery.

34. The electric vehicle, hybrid electric vehicle, or plug-in hybrid electric vehicle of claim
25 33, wherein the carbonaceous particulate material comprises a graphitic material.

35. The electric vehicle, hybrid electric vehicle, or plug-in hybrid electric vehicle of claim 33, wherein the core particles the carbonaceous particulate material comprises non-graphitic particles.

30 36. A ceramic, ceramic precursor material, or a green material comprising the surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18 as a pore forming material.

37. A dispersion comprising a liquid and a surface-modified carbonaceous particulate material comprising carbonaceous core particles with a hydrophilic non-graphitic carbon coating having a low viscosity, preferably wherein the viscosity of the

dispersion containing 40 weight% of said carbonaceous material has a viscosity of 2,000 to 4,000 mPa·s, or of 2,000 to 3,000 mPa·s, or of 2,300 to 2,600 mPa·s.

38. The dispersion according to claim 37, wherein said surface-modified carbonaceous particulate material is characterized by

5 (i) a BET SSA of less than 49 m²/g, preferably less than 25 m²/g or less than 10 m²/g; and/or
(ii) an oxygen content of greater than about 200 ppm, greater than about 400 ppm, greater than about 600 ppm, greater than about 700 ppm, or greater than about 800 ppm.

10 39. The dispersion of claim 37 or claim 38, wherein the surface-modified carbonaceous particulate material is as defined in any one of claims 1 to 10 or 18.

40. The dispersion of any one of claims 37 to 39, further comprising unmodified carbonaceous particles, wherein the surface-modified carbonaceous particles are present in an amount ranging from 10 to 99 wt. % of a total amount of carbonaceous particles, or 20 to 90 % of the total amount of carbonaceous particles, or 30 to 85 15 wt. % of the total amount carbonaceous particles.

41. The surface-modified carbonaceous particulate material as defined in any one of claims 1 to 10 or 18, or the dispersion of any one of claims 37 to 40, wherein the surface-modified carbonaceous particles have an average particle size (D₅₀) ranging 20 from 0.5 to 100 µm, or from 1 to 50 µm.