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STUDY OF BUCKYPAPER MADE OF CARBON NANOTUBES TAUNIT-4

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Abstract: Samples of buckypaper were obtained by the method of filtering suspension of carbon nanotubes Taunit-4 through a non-woven polypropylene material. Taunit-4 is few-walled carbon nanotubes with specific surface area of 600…700 m^2/g. Individual nanotubes are of 6…8 nm in diameter and are aggregated in bundles up to several tenths of a millimeter. Processing of the initial suspension of nanotubes, which improves the wetting of the surface (oxidation, addition of surfactant Triton X-100, *n*-butanol), and an increase in the duration of ultrasonic treatment results in splitting bundles of nanotubes into individual nanotubes. Apparent density of the buckypaper from Taunit-4 increases with oxidation of the nanotubes, addition of surfactant or wetting agent, increasing the duration of ultrasonic treatment.

Introduction

Buckypaper made from carbon nanotubes is a promising material [1–32], which can be used in composite materials [12, 15, 20, 22, 25], as electrode material in chemical power sources [17, 24] catalysts carrier [3], sensors [31], for shielding of electromagnetic radiation [8] and conversion of electrical energy into mechanical energy [5], as a flame retardant layer [10, 27], and in other areas. The most common method of producing buckypaper is treating of CNTs with ultrasound and filtering suspension of treated carbon nanotubes (in presence of surfactants or without them) through a microfilter. Also there is known method of buckypaper production by electrophoresis of CNTs [1, 26].

Buckypaper with the best electrical and mechanical characteristics was obtained from singlewalled (**SWNTs**) and doublewalled carbon nanotubes (**DWNTs**), due to their higher surface energy, and, as a consequence, the best binding of individual nanotubes by Van der Waals forces. SWNTs and DWNTs produced by CVD method usually are agglomerated in bundles, consisting of a number of individual nanotubes. In the process of buckypaper preparation the bundles of CNTs in the initial dispersion of nanotubes may split to a more or less extent, depending on presence of surfactants, nature of solvent and mode of ultrasonic treatment of the initial suspension. Accordingly, the properties of the resulting buckpaper vary. These issues remain poorly understood.

In the present work we have investigated the properties of buckypaper, obtained by filtration of aqueous suspension of carbon nanotubes Taunit-4, treated in different conditions.

Experimental

The starting material used for buckypaper preparation, was few-walled CNTs Taunit-4 with specific surface area of 600…700 m^2/g, average number of carbon layers of 2–4 and an average outer diameter of 6 nm. The length of the nanotubes (estimated from the length of the bundles formed by them) was up to 0.1 mm and more (Fig. 1). The Taunit-4 CNTs were obtained by CVD method on the catalyst (Fe, Co, Mo)/MgO–Al_2O_3 using acetone or propylene as a carbon source. The yield of nanotubes was 1.5–2 wt. parts from 1 wt. part of the catalyst. Purifying of nanotubes from mineral impurities (catalyst) was carried out by treatment with hydrochloric acid. The resulting aqueous suspension with CNTs mass content of 0.5 % was treated with ultrasound (1.5 l of the suspension for 1 h) using ultrasonic apparatus IL-10. This suspension was used as starting for preparation of buckypaper by filtration through a polypropylene nonwoven fabric on a Buchner funnel. After forming of the precipitate layer on the filter excess water was sucked off under vacuum, the wet layer was set between polypropylene filter material, in its turn placed between the discs of porous ceramics. The package was dried in an oven at 110 °C under pressure.

In some experiments non-ionic surfactant Triton X-100 or *n*-butanol as a wetting agent were added to the suspension of nanotubes and it was additionally treated with ultrasound for different times. The sample prepared with addition of Triton X-100 was thoroughly washed with water on filter and after drying at 110 °C was additionally kept in a ventilated oven at 200 °C to constant weight (12 h) to remove Triton. It turned out that the sample dried at 110 °C, contained about 22 % of the adsorbed Triton, despite the thorough washing of the starting material on filter.

It was studied also influence of oxidation of nanotubes with potassium permanganate on the properties of buckypaper obtained. As is known oxidation of CNTs results in appearance of phenolic, quinoid and carboxyl groups on surface of nanotubes. The oxidized nanotubes much better wetted by water. Oxidation of the surface of CNTs can be accomplished by different reagents (nitric acid, ammonium persulfate, hydrogen peroxide, sodium hypochlorite, and others). In laboratory experiments it is convenient using potassium permanganate as an oxidizing agent for CNTs in acidic medium, as the reaction proceeds rapidly and the completion of the reaction is well distinguished visually by disappearance of the permanganate color. In a typical experiment, to 150 ml of 0.5 % suspension of CNTs solution of 1 g of potassium permanganate in 150 ml of 1M sulfuric acid was added, after which the mixture was heated under stirring until disappearance of permanganate color. Then 5 g of citric acid was added and the mixture was heated to boiling for reduction of manganese dioxide, which could be produced in the system. The suspension was filtered, washed with water until neutral pH, adjusted to total volume of 300 ml, treated with ultrasound for 10 min, and then samples of buckypaper were molded on filter.

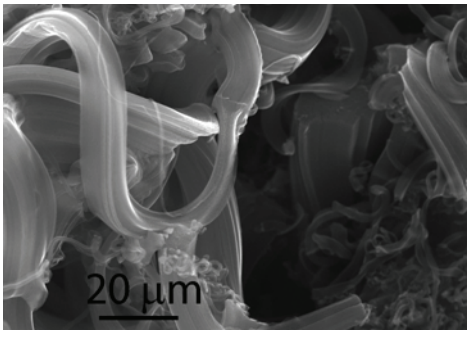

Fig. 1. SEM image of CNTs Taunit-4 as is from CVD reactor without any additional treatment

In the Table, the duration of additional treatment with ultrasound (where it took place) is assigned to the volume of suspension. That is, it was roughly assumed that at constant power of the ultrasonic emitter 100-min treatment of 1 liter of a suspension was equivalent to 5-min treatment of 50 ml

The molding conditions and properties of the buckypaper samples obtained from CNTs Taunit-4

Sample	The molding conditions		Diameter of the disk after drying in % from diameter of the initial wet sample	*h*, mm	*d*, g/cm^3
	addition of surfactant, wetting agent, additional treatment	additional treatment with ultrasound, min/l			
1	No	No	100	0.68	0.18
2	Triton X-100, 1 % in water	40	94	0.66	0.34
3	*n*-butanol, 5 vol. % in water	48	97	0.27	0.25
4		140	95	0.23	0.29
5		280	94	0.22	0.30
6	CNTs oxidized with potassium permanganate	33	Nearly 80 %, the sample cracked	0.14	0.41
7		33	78	0.31	0.56
8	The initial 0.5 % suspension of CNTs was diluted with water 1:1	No	100	0.39	0.12
9		20	100	0.29	0.18
10		60	100	0.24	0.20

Note: *h* – thickness of a sample (average from measurements in 10 points); *d* – apparent density of a sample.

of the suspension and was referred as 100 min/l. Of course, this assumption was approximate, but it could be bigger mistake to not take into account the volume of the treated suspensions.

Images of the samples were recorded using two beam scanning electron microscopy complex Neon 40, Carl Zeiss.

The thickness of samples (disks) was measured by mechanical micrometer M-0-25-0.01 in 10 points and the average was calculated.

Results and discussion

The Table shows the molding conditions and properties of the buckypaper samples obtained from CNTs Taunit-4.

From the data presented in the Table it is seen that addition of the surfactant Triton X-100 to the initial suspension of CNTs (sample 2) leads to significant increase in the apparent density of the molded paper compared to the sample 1 without surfactant. Addition to the initial suspension of CNTs *n*-butanol as a wetting agent (samples 3–5) also increases the density of the buckypaper, although to less extent than with the Triton. The greatest increase in density was achieved by oxidation of the initial CNTs with potassium permanganate (sample 6). Linear shrinkage along the plane of the samples after drying was the greater the greater the greater the density of a sample. All these facts can be explained if we take into account that the presence of surfactants, wetting agents or grafting of polar groups to the surface of carbon nanotubes by oxidation facilitates sliding of the nanotubes and their bundles while molding an

aqueous slurry on the filter, resulting in more dense packing of nanotubes. The same effect was caused by increase of treatment time of nanotubes suspension by ultrasound. High density and very large shrinkage during drying of buckypaper samples obtained from oxidized nanotubes most likely was caused by contraction of nanotubes by capillary forces.

To determine the extent to which bundles of nanotubes present in the original nanotubes Taunit-4, remain while molding of buckypaper, we have studied the samples of buckypaper using scanning electron microscope.

As can be seen from Fig. 2, buckypaper, obtained from the initial suspension of the CNTs Taunit-4 (sample 1), consists of long intertwined bundles of nanotubes. Each bundle consists of many individual nanotubes. Thus, treatment of the initial suspension of CNTs with ultrasound did not lead to a significant splitting of the bundles into individual nanotubes.

As can be seen from Fig. 2, the length of fragments of some bundles emerging to the surface and entering into the field of view is greater than 100 microns. If we assume that nanotubes have the same length as the bundles, their length can be several tenths of millimeter, i.e., macroscopic. One can also see from Fig. 2 that individual nanotubes in bundles have spiral shape to different extent. It can be assumed that such shape of nanotubes arises because of inhomogeneity of catalyst surface and different rate of growth of individual nanotubes. Those nanotubes, which grow more slowly, are stretched and define the length of the bundle. However, some of the nanotubes grow faster and thus form a spiral shape. Probably the entire bundle is an elastic formation, as is evidenced by characteristic folds on the bend fragments (Fig. 1, top left corner).

Macroscopic length of the nanotubes Taunit-4 is proved also by behavior of their agglomerates in aqueous dispersion. If you attempt to loosen them by glass rod the agglomerates behave like wet cotton wads.

Additional treatment of the suspension by ultrasound (sample 10) led to partial dissagregation of the nanotube bundles (Fig. 3).

Fig. 4 shows SEM images of buckypaper, molded from nanotubes, oxidized with potassium permanganate (sample 6). It is evident that oxidation in conjunction with action of ultrasound in aqueous suspension leads to disaggregation of bundles into individual nanotubes, due to better wettability of oxidized nanotubes with water. After drying of the wet buckypaper layer molded on filter structure with much greater apparent density formed compared to untreated nanotubes, because of contraction of nanotubes by capillary forces. The nanotubes in the resulting buckypaper are arranged predominantly chaotically.

For the sample 2 of buckypaper obtained with treating the suspension of Taunit-4 by ultrasound in presence of surfactant (Triton X-100), most of bundles are randomized (Fig. 5), possibly in a little less extent than for the sample oxidized with permanganate.

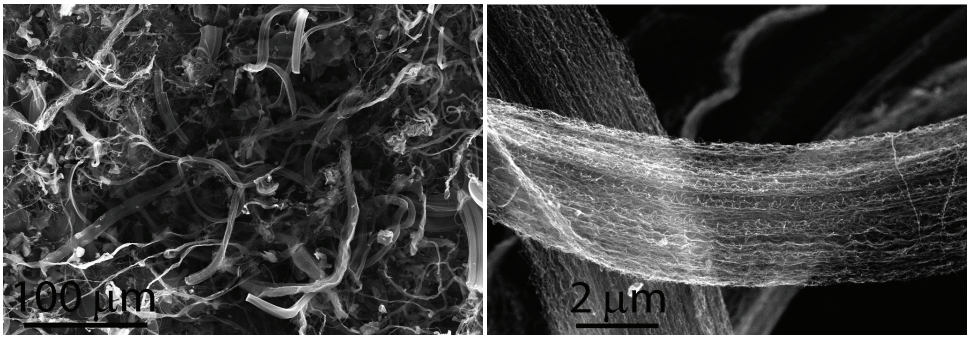

Fig. 2. Images (SEM) of buckypaper molded from aqueous suspension of Taunit-4 without any additional processing

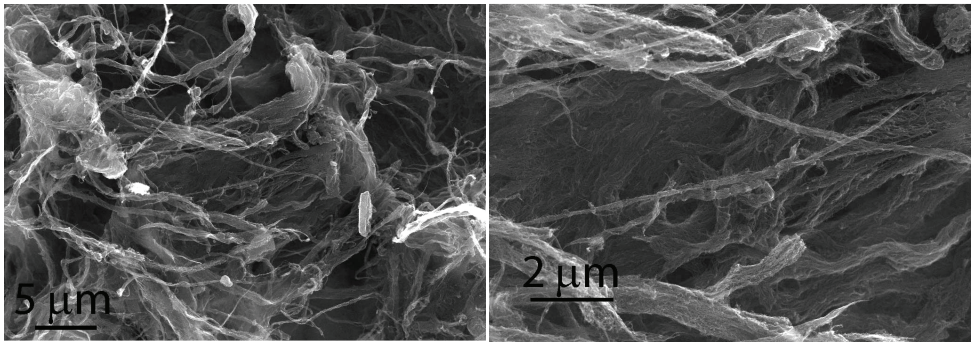

Fig. 3. Images (SEM) of buckypaper from CNTs Taunit-4 molded with additional processing of the initial suspension by ultrasound

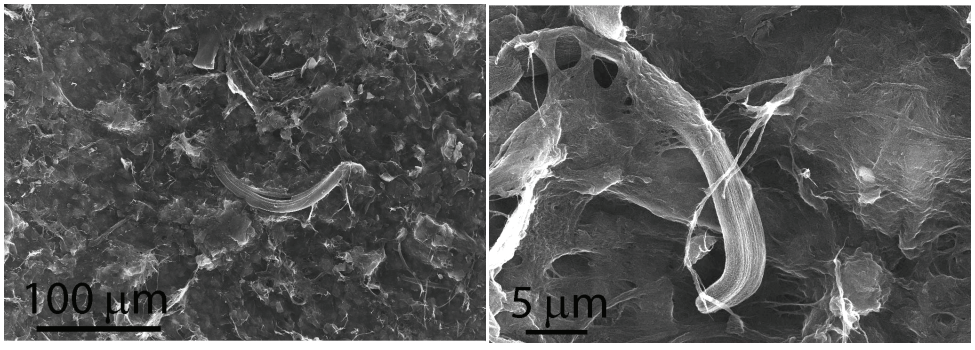

Fig. 4. Images (SEM) of buckypaper, molded from aqueous suspension of nanotubes Taunit-4, oxidized with potassium permanganate in acidic medium

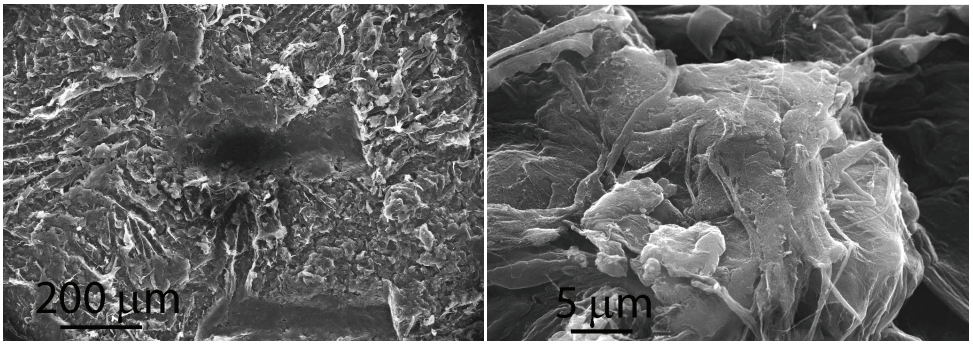

Fig. 5. Images (SEM) of buckypaper, molded from aqueous suspension of nanotubes Taunit-4 treated with ultrasound in presence of surfactant Triton X-100

Almost the same result was achieved by treatment of the suspension of Taunit-4 with ultrasound in presence of *n*-butanol, which in this case improves the wetting of nanotube surface with water (Fig. 6).

Thus, treatment of the initial suspension of nanotubes, which improves the wetting of the surface of nanotubes (oxidation, addition of surfactant, *n*-butanol), and increasing the duration of ultrasound treatment allows breaking bundles of nanotubes into individual nanotubes. This provides more dense packing of nanotubes in the final buckypaper. However, one should note that in this paper the initial suspensions of nanotubes, which were used for molding buckypaper, were sufficiently concentrated (0.25–0.5 %). At such concentration in any case nanotubes are agglomerated. In order to

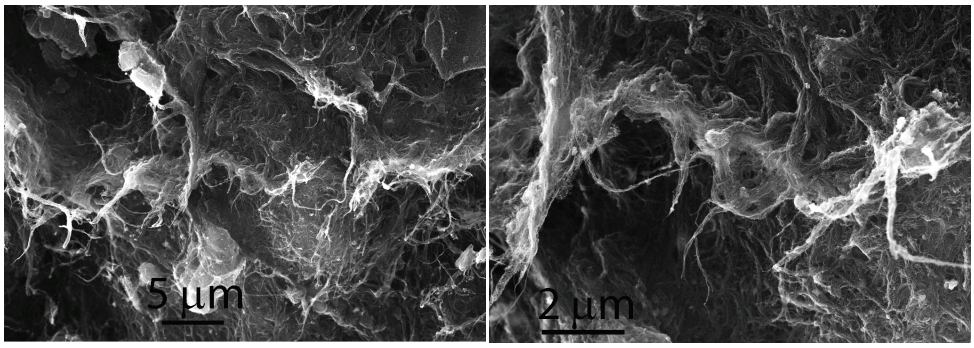

Fig. 6. Images (SEM) of buckypaper, molded from aqueous suspension of nanotubes Taunit-4, with addition of *n*-butanol and treatment with ultrasound

obtain the "true" solutions of nanotubes (not agglomerated) in water, even in presence of surfactants, the mass concentration of nanotubes should not exceed a few hundredths and even thousandths of %. It is obvious that buckypaper with regular structure with best mechanical properties can be obtained from the "true" solution of nanotubes by molding a layer of buckypaper on micro-filter or by method of electrophoresis. However, the buckypaper obtained by methods described above, the structure of which is formed by bundles of nanotubes or their agglomerates, can be useful for applications where rapid diffusion of the reagents or ions in a layer of buckypaper is desirable. In fact, the samples of buckypaper from Taunit-4 are materials with bimodal porosity, where there are nanometer-sized pores (between individual nanotubes in bundles or agglomerates), and macropores between the agglomerates or bundles. Such materials can be effective for creation chemical power sources, catalysts, sensors, and for other similar applications.

Conclusion

1. Samples of buckypaper from carbon nanotubes Taunit-4 were obtained by method of filtering aqueous suspension of nanotubes through a non-woven polypropylene material.

2. Apparent density of the buckypaper made from CNTs Taunit-4 increases with oxidation of nanotubes, addition of surfactant or wetting agent, increasing the processing time of the suspension by ultrasound.

3. Processing of the initial suspension of nanotubes, which improves wetting of the surface of nanotubes (oxidation, addition of surfactant, n-butanol), and increase of duration of treatment with ultrasound facilitates breaking the bundles of nanotubes into individual nanotubes.

References

1. Buckypaper Fabrication by Liberation of Electrophoretically Deposited Carbon Nanotubes / J.L. Rigueur [et al.] // Carbon. – 2010. – Vol. 48. – P. 4090–4099.

2. Nanotechnology: 'Buckypaper' from Coaxial Nanotubes / M. Endo [et al.] // Nature. – 2005. – Vol. 433. – P. 476.

3. Buckypaper-Based Catalytic Electrodes for Improving Platinum Utilization and PEMFC's Performance / W. Zhu [et al.] // Electrochimica Acta. – 2010. – Vol. 55. – P. 2555–2560.

4. Functionalization of Carbon Nanotubes by Electrochemical Reduction of Aryl Diazonium Salts: A Bucky Paper Electrode / J.L. Bahr [et al.] // J. Am. Chem. Soc. – 2001. – Vol. 123. – P. 6536–6542.

5. Carbon Nanotubes Acting Like Actuators / J. Fraysse [et al.] // Carbon. – 2002. – Vol. 40. – P. 1735–1739.

6. Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films / H.-Z. Geng [et al.] // J. Amer. Chem. Soc. – 2007. – Vol. 129. – P. 7758–7759.

7. Effects of Surfactants and Alignment on the Physical Properties of Single-Walled Carbon Nanotube Buckypaper / J.G. Park [et al.] // J. Appl. Phys. 106, 104310 (2009).

8. Electromagnetic Interference Shielding Properties of Carbon Nanotube Buckypaper Composites / J.G. Park [et al.] // Nanotechnology. – 2009. – Vol. 20. – P. 415702.

9. Fabrication of High-Purity, Double-Walled Carbon Nanotube Buckypaper / Y.A. Kim [et al.] // Chem. Vap. Deposition. – 2006. – Vol. 12. – P. 327–330.

10. Fire Retardancy of a Buckypaper Membrane / Q. Wu [et al.] // Carbon. – 2008. – Vol. 46. – P. 1164–1165.

11. Geometric Control and Tuneable Pore Size Distribution of Buckypaper and Buckydiscs / R.L.D. Whitby [et al.] // Carbon. – 2008. – Vol. 46. – P. 949–956.

12. High CNT Content Composites with CNT Buckypaper and Epoxy Resin Matrix: Impregnation Behaviour Composite Production and Characterization / P.E. Lopes [et al.] // Composite Structures. – 2010. – Vol. 92. – P. 1291–1298.

13. Highly Oriented Carbon Nanotube Papers Made of Aligned Carbon Nanotubes / D. Wang [et al.] // Nanotechnology. – 2008. – Vol. 19. – P. 075609.

14. High-Purity Diamagnetic Single-Wall Carbon Nanotube Buckypaper / Y. Kim [et al.] // Chem. Mater. – 2007. – Vol.19. – P. 2982–2986.

15. Improving the Mechanical Properties of Single-Walled Carbon Nanotube Sheets by Intercalation of Polymeric Adhesives / J.N. Coleman [et al.] // Applied Physics Letters. – Vol. 82. – P. 1682–1684.

16. Cranford, S.W. In Silico Assembly and Nanomechanical Characterization of Carbon Nanotube Buckypaper / S.W. Cranford, M.J. Buehler // Nanotechnology. – 2010. – Vol. 21. – P. 265706, 201.

17. Lithium–Air Batteries Using SWNT/CNF Buckypapers as Air Electrodes / G.Q. Zhang [et al.] // Journal of The Electrochemical Society. – 2010. – Vol. 157. – P. A953–A956.

18. Mechanical and Electrical Properties of Polycarbonate Nanotube Buckypaper Composite Sheets / G.T. Pham [et al.] // Nanotechnology. – 2008. – Vol. 19. – P. 325705.

19. Mechanical Modelling of Carbon Nanomaterials from Nanotubes to Buckypaper / M.M. Zaeri [et al.] // Carbon. – 2010. – Vol. 48. – P. 3916–3930.

20. Processing and Property Investigation of Single-Walled Carbon Nanotube (SWNT) Buckypaper/Epoxy Resin Matrix Nanocomposites / Z. Wang [et al.] // Composites Part A: Applied Science and Manufacturing. – 2004. – Vol. 35. – P. 1225–1232.

21. Pyroelectric Temperature Sensitization of Multi-Wall Carbon Nanotube Papers / A. Kukovecz [et al.] // Carbon. – 2008. – Vol. 46. – P. 1262–1265.

22. Gou, J. Single-Walled Nanotube Bucky Paper and Nanocomposite / J. Gou // Polymer International. – 2006. – Vol. 55. – P. 1283–1288.

23. Structural Changes and Raman Analysis of Single-Walled Carbon Nanotube Buckypaper after High Current Density Induced Burning / J.G. Park [et al.] // Carbon. – 2008. – Vol. 46. – P. 1175–1183.

24. Ultra-Low Platinum Loading High-Performance PEMFCs Using Buckypaper-Supported Electrodes / W. Zhu [et al.] // Electrochemistry Communications. – 2010. – Vol. 12. – P. 1654–1657.

25. Correlation between Young's Modulus and Impregnation Quality of Epoxy-Impregnated SWCNT Buckypaper / B. Ashrafi [et al.] // Composites. Part A: Applied Science and Manufacturing. – 2010. – Vol. 41. – P. 1184–1191.

26. Buckypaper Fabrication by Liberation of Electrophoretically Deposited Carbon Nanotubes / J.L. Rigueur [et al.] // Carbon. – 2010. – Vol. 48. – P. 4090–4099.

27. Carbon Nanotube Buckypaper to Improve Fire Retardancy of High-Temperature/High-Performance Polymer Composites / X. Fu [et al.] // Nanotechnology. – 2010. – Vol. 21. – P. 235701.

28. Comparison of the Electrochemical Behaviour of Buckypaper and Polymer-Intercalated Buckypaper Electrodes / S. Ounnunkad [et al.] // Journal of Electroanalytical Chemistry. – 2011. – Vol. 652. – P. 52–59.

29. Li, Y. A Theoretical Evaluation of the Effects of Carbon Nanotube Entanglement and Bundling on the Structural and Mechanical Properties of Buckypaper / Y. Li, M. Kröger // Carbon, Available online 19 December 2011, In Press, Corrected Proof.

30. Zhang, J. Influence of Geometries of Multi-Walled Carbon Nanotubes on the Pore Structures of Buckypaper / J. Zhang, D. Jiang // Composites. Part A: Applied Science and Manufacturing. – 2012. – Vol. 43. – P. 469–474.

31. Rein, M.D. Sensors and Sensitivity: Carbon Nanotube Buckypaper Films as Strain Sensing Devices / M.D. Rein, O. Breuer, H.D. Wagner // Composites Science and Technology. – 2011. – Vol. 71. – P. 373–381.

32. Yue, Y. Thermal Transport in Multiwall Carbon Nanotube Buckypapers / Y. Yue, X. Huang, X. Wang // Physics Letters A. – 2010. – Vol. 374. – P. 4144–4151.

Исследование углеродной бумаги из нанотрубок Таунит-4

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Ключевые слова и фразы: поверхностно-активное вещество; Таунит-4; углеродная бумага; углеродные нанотрубки; ультразвук.

Аннотация: Методом фильтрования суспензии нанотрубок через нетканый полипропиленовый материал получены образцы бумаги из углеродных нанотрубок Таунит-4, представляющих собой малослойные нанотрубки с удельной поверхностью 600…700 $м^2/г$. Индивидуальные нанотрубки диаметром 6…8 нм собраны в пучки длиной до нескольких десятых долей миллиметра. Обработка исходной суспензии нанотрубок, улучшающая смачивание их поверхности (окисление, добавка ПАВ Тритон Х-100, *н*-бутанола), и увеличение продолжительности обработки ультразвуком позволяют расщепить пучки нанотрубок на индивидуальные нанотрубки. Кажущаяся плотность бумаги из Таунита-4 увеличивается при окислении нанотрубок, добавке ПАВ или смачивателя, увеличении времени обработки суспензии ультразвуком.

Forschung des Kohlenstoffpapiers aus den Nanoröhren Taunit-4

Zusammenfassung: Von der Methode der Filterung der Suspension der Nanoröhren durch das nichtgewebte Polypropylenmaterial sind die Muster des Papiers aus den Kohlenstoffnanoröhren Taunit-4, die die schichtarmen Nanoröhre mit der

spezifischen Oberfläche 600…700 m^2/g darstellen, erhalten. Die individuellen Nanoröhre mit dem Durchmesser 6…8 nm sind in die Bündel von der Länge bis zu einigen zehnten Anteil des Millimeters gesammelt. Die Bearbeitung der Ausgangssuspension der Nanoröhre, die das Anfeuchten ihrer Oberfläche verbessert (die Oxydierung, der Zusatz von Tenside Triton X-100, *n*-Butanol), und die Vergrößerung der Dauer der Bearbeitung vom Ultralaut lassen die Bündel der Nanoröhre auf die individuellen Nanoröhre zu spalten. Die scheinende Dichte des Papiers aus Taunit-4 vergrössert sich bei der Oxydierung der Nanoröhre, bei dem Zusatz von Tenside oder vom Befeuchter, bei der Vergrößerung der Zeit der Bearbeitung der Suspension durch den Ultraschall.

Etude du papier carbonique à partir des nanotubes Taunit-4

Résumé: Par la méthode du filtrage de la matière en suspension des nanotubes à partir un matériel polypropylène non-tissé sont reçus les exemples du papier carbonique à partir des nanotubes Taunit-4 présentant les nanotubes de peu de couches avec une surface spécifique de 600…700 m^2/g. Les nanotubes individuels du diamètre de 6…8 nm sont ramassés en faisceau de la longeur de quelques dixièmes du millimètre. Le traitement de la suspension initiale des nanotubes améliorant l'arrosage de la surface (oxydation, addition du surfactant Triton X-100, *n*-butanol) et l'augmentation de longévité du traitement par l'ultrason permettent de désagréger les faisceaux des nanotubes sur ceux individuels. La densité apparente du papier augmente lors de l'oxydation des nanotubes, l'addition du surfactant ou du mouillanté, l'augmentation du temps du traitement de la suspension par l'ultrason.

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