Short communication

Lignin-based multiwall carbon nanotubes

Wolfgang Gindl-Altmutter[a,*], Janea Köhnke[a], Christoph Unterweger[b], Notburga Gierlinger[c], Jozef Keckes[d], Jakub Zalesak[d], Orlando J. Rojas[e]

[a] Department of Materials Science and Process Engineering, BOKU-University of Natural Resources and Life Science, Vienna, A-3430 Tulln, Austria
[b] Wood K puls – Kompetenzzentrum Holz GmbH, A-4040 Linz, Austria
[c] Department of Nanobiotechnology, BOKU-University of Natural Resources and Life Science, Vienna, A-1190 Vienna, Austria
[d] Department of Materials Physics, Montanuniversität of Leoben, A-8700 Leoben, Austria
[e] Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland

ABSTRACT

Carbon particles were produced by carbonization of perfectly spherical, sub-micron beads obtained from Kraft lignin. While the bulk of the particles consisted of carbon with only moderate structural order, high-resolution transmission electron microscopy revealed the presence of highly ordered multilayered carbon structures adhering to the surface of the carbon spheres. Besides irregularly shaped multiwall carbon, well-defined multiwall carbon nanotubes were identified. Energy dispersive x-ray analysis hints at a catalytic action of metallic impurities present in lignin in the synthesis of these lignin-based carbon nanostructures. Lignin-based multiwall carbon nanotubes are considered of high interest with regard to providing bio-based alternatives for fossil-based high-performance materials.

1. Introduction

The wood polymers cellulose, hemicellulose, and lignin are the most abundant renewable resources for bio-based materials. Wood-based materials are widely used in construction and furniture, and wood-derived cellulose fibers are the basis of pulp, paper, and spun cellulose. Due to the inherent nano-fibrous architecture of cellulose, nano-objects such as cellulose nanofibers and cellulose nanocrystals are produced in a straightforward manner [1] and numerous potential applications for this biobased nanomaterials are being discussed [2–5]. Lignin is second to cellulose in abundance and technical lignins arise as a by-product of the pulping process. Depending on the chemical process used for the delignification of wood, the structure of technical lignins is highly variable. At present, lignin is still mainly combusted for the generation of heat, energy, and steam, and little used for materials, the only major exception being lignosulfonate [6]. Consequently, research into high-value applications for lignin is intense, with applications being discussed in bioaromatics, biopolymers, or biofuel [7–10]. Compared to the linear polysaccharide cellulose, the most important structural difference of lignin is its amorphous polyaromatic structure [11]. Due to the favorable ratio of carbon and oxygen in lignin compared to cellulose [12], lignin-derived carbon is an attractive high-value product, e.g. in the shape of carbon fiber produced from melt-spun lignin [13,14],

electrospun carbon nanofiber [15], carbon particles [16], and activated carbon [17]. Lignin, on the contrary, is amorphous in structure, which complicates the synthesis of nanomaterials thereof, particularly when high aspect ratio objects with well-ordered structure such as e.g. carbon nanotubes are desired. While particulate (spherical) lignin nanoparticles were synthesized repeatedly [12,18,19], elongated lignin-based nano-objects are mainly described in terms of electrospun lignin fiber [20–22]. In the present study we report the discovery of highly ordered lignin based carbon nano-objects which differ significantly from the examples cited above.

2. Experimental

With the aim of obtaining electrically conductive carbon, Kraft lignin (Indulin AT)-derived nanospheres [12] were subjected to thermostabilization and subsequent carbonization in inert atmosphere up to a temperature of 2000 °C following a protocol described in detail elsewhere [23]. Briefly, the procedure involved the generation of small droplets of lignin solution in dimethylformamide via a jet atomizer that used nitrogen gas as carrier, subsequent drying in a heated laminar flow reactor, and fractionation with a low-pressure impactor. The bulk of the resulting carbon powder was characterized by means of Raman spectroscopy (alpha300RA, WITec GmbH, Germany, laser λ = 532 nm) and

* Corresponding author.
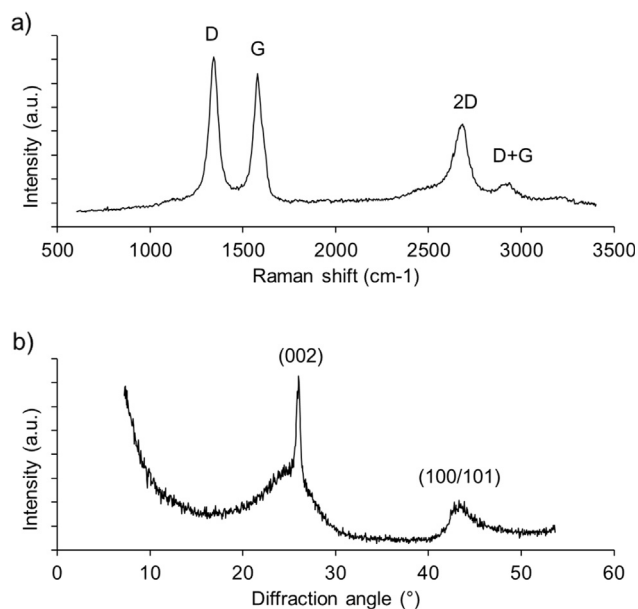 *E-mail address:* wolfgang.gindl@boku.ac.at (W. Gindl-Altmutter).

Fig. 1. Raman spectroscopy (a) and x-ray diffraction (b) of lignin-derived carbon particles.

x-ray diffraction (Rigaku SmartLab 5-Axis X-ray diffractometer using glass capillaries and Cu K alpha radiation λ = 0.15418 nm). Samples for Transmission electron microscopy (TEM) were prepared by dispersion of heat-treated samples onto TEM carbon support grids. TEM imaging was performed using a CS-corrected FEI Titan Themis equipped with a Wien filter monochromator. The microscope was operated at accelerating voltage of 60 kV with excited monochromator. Images were taken under slight defocus at short exposure times with a Ceta CMOS camera. Collection of energy-dispersive X-ray spectroscopy (EDX) maps was performed in scanning TEM mode at accelerating voltage of 200 kV with a beam current of 0.5 nA. The data was treated using built-in standards in FEI Velox software.

3. Results and discussion

Carbonization resulted in an overall gravimetric yield of 25% carbon material based the initial mass of lignin used as a raw material. Raman spectroscopy of the carbonized material (Fig. 1a) reveals four prominent bands [24,25]. The D-band at ~1350 cm^{-1} represents signal from a disordered graphitic lattice. Its second order harmonic 2D appears at ~2700 cm^{-1}. A strong G band at ~1580^{-1} indicative of a highly ordered graphitic lattice, and a weak D + G band at ~2910 cm^{-1} are also found. The ratio ID/IG may be used as a measure of structural imperfections and impurities in carbon materials. It is < < 1 for structurally perfect graphene, perfect graphite or carbon nanotubes [26,27]. In the present study and similar studies on carbonized lignin, ID/IG is close to one [28], indicating the presence of ordered graphitic domains, but also abundant disordered regions. X-ray diffraction (Fig. 1b) confirms this finding. Here, the most important feature is a broad peak associated with amorphous carbon between scattering angles 20–30°, and the well-defined 0 0 2 diffraction peak at 26° originating from the stacking of graphene sheets in graphite [29]. As a result of comparably poor structural order, the electrical resistivity of the carbon powder produced in the present study measured according to Ref. [30] was high with ~0.04–0.1 Ωm. Compared to ~0.004–0.025 Ωm for electrically conducting carbon black [30], which is regularly used as filler in conduction polymer composites, this value is rather high unsatisfying. Thus, the aim of achieving highly conductive carbon was not achieved. Nonetheless, further inspection of carbon particles revealed interesting structural features. Transmission electron microscopy (Fig. 2) showed a perfectly spherical shape for individual particles, which were 83 ± 52 nm in diameter. Furthermore, agglomeration of elements protruding from to the surface of the carbon spheres was identified, as depicted with higher magnification in Fig. 2b. These objects typically show lengths of several hundreds of nm and widths of 100–200 nm and consist of needle-shaped filaments together with irregular features between the nano-needles. High resolution images reveal domains of highly ordered carbon for both regions (Fig. 3). The bulk of the objects shown in Fig. 2b consist of multiply kinked and occasionally spherical arrangements of multiwall carbon structures with ~10–20 graphene layers (Fig. 3a). The straight needle-shaped filaments visible in Fig. 2b are up to 400 nm long and 14 nm in diameter. They are identified as multiwall carbon nanotubes with ~16 layers of graphene in Fig. 3b.

Reports on carbon nanotube structures synthesized from bio-based resources are sparse. Using thermo-oxidative treatment at temperatures up to 400 °C, apparent carbon nanotubes were synthesized from wood fibers [31]. Microwave plasma-irradiation of rice husk led to variably structured nanocarbon [32]. Using wood sawdust as a source of carbon, carbon nanostructures were synthesized in a tubular reactor using an Fe/Mo/MgO catalyst [33]. Metal-catalyzed formation of carbon nanostructures, specifically multi-layer graphene encapsulated metal nanoparticles was also reported for lignin [34]. Since elongated structures with dimensions similar to carbon nanotubes may also arise from non-
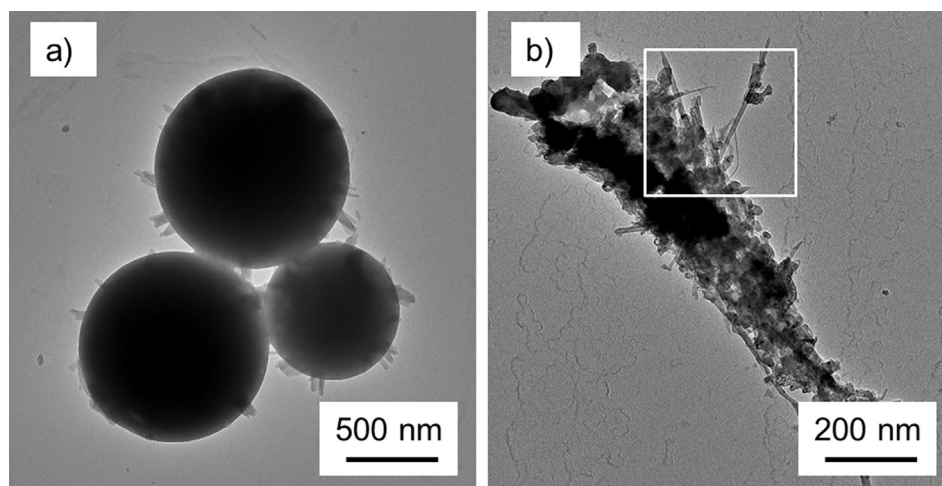

Fig. 2. Representative transmission electron microscopy of lignin-derived carbon particles shown at two magnifications (a and b). The higher magnification (b) shows an example of irregularly shaped graphitic structures emerging from the surface of spherical carbon particles (a).
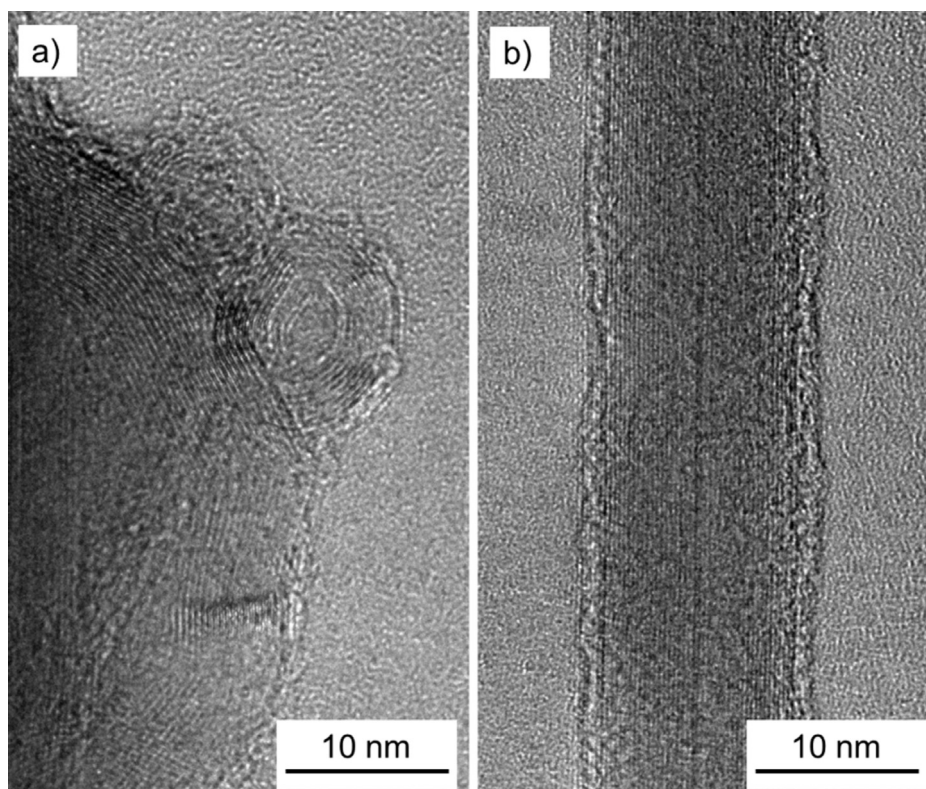
Fig. 3. Irregular-shaped and multiply kinked multilayer carbon structures (a) and well-aligned multiwall carbon nanotube (b).

carbon materials, as is the case for silica nano-needles in carbonized grass lignin [35], transmission electron microscopy in combination with energy-dispersive x-ray analysis (TEM-EDX) was also carried out. In addition to clear identification of carbon nanostructures, such an analysis may also help elucidating potential mechanisms responsible for carbon nanotube synthesis in the present study.

In a first TEM-EDX experiment, the region designated with a white rectangle in Fig. 2b, consisting of a number of nanotubes together with geometrically not clearly defined globular elements was analyzed. As shown in Fig. 4a TEM-EDX reveals strong signals for carbon, oxygen, and silica. While it is reasonable that carbon and oxygen give strong signal from the entire specimen (Fig. b-c), the silica signal is most probably not originating from the sample, since the raw material Kraft lignin (Indulin AT) only contains trace amounts of silica [11], but from the detector in the TEM, which is made of silica. Disregarding the copper signal originating from the specimen holder, minor signals were identified for magnesium, phosphorus, sulfur, and potassium, which all occur to varying amounts in the raw material Indulin AT [11]. On the one hand, the TEM-EDX results provide clear proof that the structures observed are indeed carbon nanostructures. On the other hand, the element map for Mg gives some indication for a potential mechanism responsible for carbon nanotube synthesis. In contrast to carbon and oxygen, magnesium is unevenly distributed throughout the specimen volume and, at least in one case (arrow in Fig. 4d) agglomerated at the base of a carbon nanotube. During the carbonization of lignin at temperatures up to 2000 °C as carried out in the present study, a significant amount of carbon monoxide is liberated [28]. In combination with metallic impurities in the lignin acting as catalyst, conditions enabling the formation of carbon nanotubes may arise [36,37]. In the present study, no metallic catalyst was added to the lignin prior to carbonization, but inorganic impurities, in particular magnesium were detected, which can be found in small amounts of $140 \, \text{mg} \, \text{kg}^{-1}$ in the lignin used as raw material for the present study [11]. As to the location of magnesium at the base of carbon nanotubes, Fig. 5 provides additional evidence. Here, a multiwall carbon nanotube attached to a spherical

structure is shown. The multiwall nanotube consists of an outer region of repeatedly kinked multilayer graphene and an inner region of amorphous carbon. The elemental composition of this individual nanotube as shown in Fig. 5b and c is essentially carbon, with a surface rich in oxygen. Very clearly, the elemental composition of the sphere attached to the carbon nanotube differs in that it shows no carbon signal, but a clear magnesium signal in addition to oxygen. Since a catalytic role in the synthesis of carbon nanotubes by means of thermal chemical vapor deposition was established for magnesium [37,38], we propose that inorganic metallic impurities in lignin may serve as catalysts promoting the formation of carbon nanotubes during carbonization experiments. Interestingly, the temperature-induced segregation of inorganic compounds from biomass into metal nanoparticles capable of catalysing the growth of carbon nanotubes has already been proposed as a mechanism to explain the presence of carbon nanotubes in ancient Damascus steel [39].

4. Conclusion

In summary, it was clearly proved that multiwall carbon nanostructures may occur during the carbonization of technical lignin. Furthermore, experimental evidence hints at a catalytic role of magnesium in carbon nanotube synthesis. The lignin-based carbon nanostructures found in the present study are of significant interest with regard to potential novel synthesis pathways of bio-based carbon and high-value materials derived thereof.
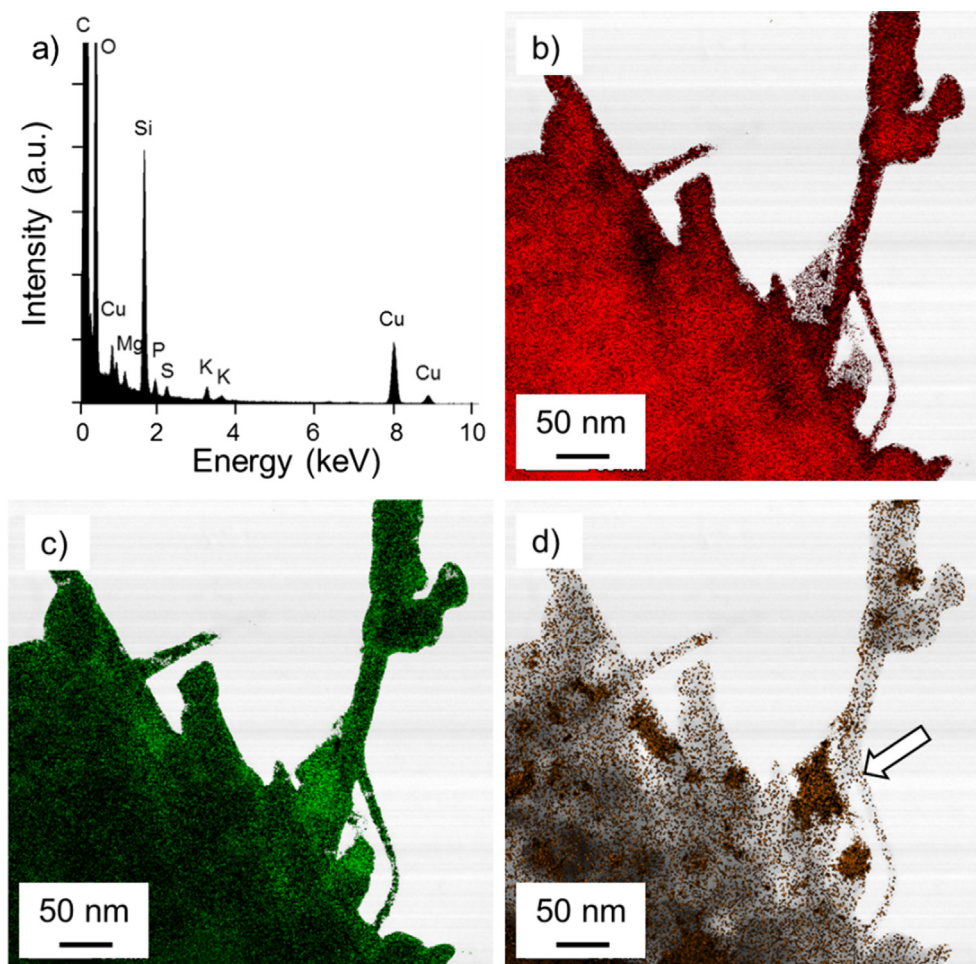
Fig. 4. Results of TEM-EDX in the region of interest designated with a white rectangle in Fig. 2b (a) and element maps for carbon (b), oxygen (c), and magnesium (d). The element maps were digitally enhanced by subtracting background signal.
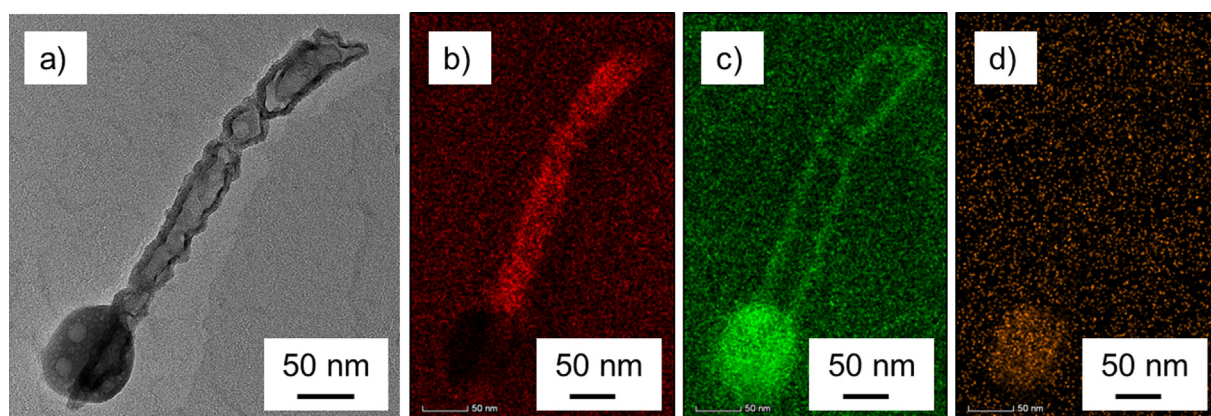

Fig. 5. TEM image of a multiwall carbon nanotube emerging from a spherical structure (a) together with TEM-EDX element maps for carbon (b), oxygen (c), and magnesium (d).

References

[1] Dufresne A. Nanocellulose: a new ageless bionanomaterial. Mater Today 2013;16:220–7.

[2] Klemm D, Kramer F, Moritz S, Lindstrom T, Ankerfors M, Gray D, et al. Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed 2011;50:5438–66.

[3] Isogai A. Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. J Wood Sci 2013;59:449–59.

[4] Charreau H, Foresti ML, Vázquez A. Nanocellulose patents trends: a comprehensive review on patents on cellulose nanocrystals, microfibrillated and bacterial cellulose.

Rec Pat Nanotechnol 2013;7:56–80.

[5] Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, et al. Current international research into cellulose nanofibres and nanocomposites. J Mater Sci 2010;45:1–33.

[6] Rojas OJ, Bullon J, Ysambertt F, Forgiarini A, Salager J-L, Argyropoulos DS. Lignins as emulsion stabilizers. In: Argyropoulos DS, editor. Materials, chemicals, and energy from forest biomass. 1155 Sixteenth St Nw, Washington, Dc 20036, USA: Amer Chemical Soc; 2007. p. 182–99.

[7] Laurichesse S, Avérous L. Chemical modification of lignins: Towards biobased polymers. Prog Polym Sci 2014;39:1266–90.

[8] Schutyser W, Renders T, Van den Bosch S, Koelewijn SF, Beckham GT, Sels BF. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem Soc Rev 2018;47:852–908.

[9] Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, Davison BH, Dixon RA, Gilna P, Keller M, Langan P, Naskar AK, Saddler JN, Tschaplinski TJ, Tuskan GA, Wyman CE. Lignin valorization: improving lignin processing in the biorefinery. Science 2014;344:1246843.

[10] Laskar DD, Yang B, Wang HM, Lee J. Pathways for biomass-derived lignin to hydrocarbon fuels. Biofuels Bioprod Biorefining 2013;7:602–26.

[11] Constant S, Wienk HLJ, Frissen AE, Peinder PD, Boelens R, van Es DS, Grisel RJH, Weckhuysen BM, Huijgen WJJ, Gosselink RJA, Bruijnincx PCA. New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chem 2016;18:2651–65.

[12] Ago M, Huan S, Borghei M, Raula J, Kauppinen EI, Rojas OJ. High-throughput synthesis of lignin particles (similar to 30 nm to similar to 2 mu m) via aerosol flow reactor: Size fractionation and utilization in pickering emulsions. ACS Appl Mater Interfaces 2016;8:23302–10.

[13] Baker DA, Rials TG. Recent advances in low-cost carbon fiber manufacture from lignin. J Appl Polym Sci 2013;130:713–28.

[14] Kadla JF, Kubo S, Venditti RA, Gilbert RD, Compere AL, Griffith W. Lignin-based carbon fibers for composite fiber applications. Carbon 2002;40:2913–20.

[15] Ruiz-Rosas R, Bedia J, Lallave M, Loscertales IG, Barrero A, Rodríguez-Mirasol J, et al. The production of submicron diameter carbon fibers by the electrospinning of lignin. Carbon 2010;48:696–705.

[16] Pang J, Zhang WF, Zhang JL, Zhang HM, Cao GP, Han MF, et al. Oxygen and nitrogen co-enriched sustainable porous carbon hollow microspheres from sodium lignosulfonate for supercapacitors with high volumetric energy densities. Chemelectrochem 2018;5:1306–20.

[17] Rodríguez Correa C, Stollovsky M, Hehr T, Rauscher Y, Rolli B, Kruse A. Influence of the carbonization process on activated carbon properties from lignin and lignin-rich biomasses. ACS Sus Chem Eng. 2017;5:8222–33.

[18] Beisl S, Miltner A, Friedl A. Lignin from micro- to nanosize: production methods. Int J Mol Sci 2017;18:1244.

[19] Xiong FQ, Han YM, Wang SQ, Li GY, Qin TF, Chen Y, et al. Preparation and formation mechanism of size-controlled lignin nanospheres by self-assembly. Ind Crops Prod 2017;100:146–52.

[20] Ago M, Okajima K, Jakes JE, Park S, Rojas OJ. Lignin-based electrospun nanofibers reinforced with cellulose nanocrystals. Biomacromolecules 2012:13918–26.

[21] Cho M, Karaaslan M, Chowdhury S, Ko F, Renneckar S. Skipping oxidative thermal stabilization for lignin-based carbon nanofibers. ACS Sus Chem Eng 2018:66434–44.

[22] Zhao Y, Liu Y, Tong CC, Ru J, Geng BY, Ma ZQ, et al. Flexible lignin-derived electrospun carbon nanofiber mats as a highly efficient and binder-free counter electrode for dye-sensitized solar cells. J Mater Sci 2018;53:7637–47.

[23] Gindl-Altmutter W, Fürst C, Mahendran AR, Obersriebnig M, Emsenhuber G, Kluge M, et al. Electrically conductive kraft lignin-based carbon filler for polymers. Carbon 2015;89:161–8.

[24] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman microspectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. Carbon 2005;43:1731–42.

[25] Zdrojek M, Gebicki W, Jastrzebski C, Melin T, Huczko A. Studies of multiwall carbon nanotubes using Raman spectroscopy and atomic force microscopy. Solid State Phen 2004;99–100:265–8.

[26] Heise HM, Kuckuk R, Ojha AK, Srivastava A, Srivastava V, Asthana BP. Characterisation of carbonaceous materials using Raman spectroscopy: a comparison of carbon nanotube filters, single- and multi-walled nanotubes, graphitised porous carbon and graphite. J Raman Spec 2009;40:344–53.

[27] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, et al. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. Nano Lett 2009;9:30–5.

[28] Köhnke J, Rennhofer H, Lichtenegger H, Mahendran AR, Unterweger C, Prats-Mateu B, et al. Electrically conducting carbon microparticles by direct carbonization of spent wood pulping liquor. ACS Sus Chem Eng 2018;6:3385–91.

[29] Li ZQ, Lu CJ, Xia ZP, Zhou Y, Luo Z. X-ray diffraction patterns of graphite and turbostratic carbon. Carbon 2007;45:1686–95.

[30] Sánchez-González J, Macías-García A, Alexandre-Franco MF, Gómez-Serrano V. Electrical conductivity of carbon blacks under compression. Carbon 2005;43:741–7.

[31] Goodell B, Xie X, Qian Y, Daniel G, Peterson M, Jellison J. Carbon nanotubes produced from natural cellulosic materials. J Nanosci Nanotechnol 2008;8:2472–4.

[32] Wang Z, Ogata H, Morimoto S, Ortiz-Medina J, Fujishige M, Takeuchi K, et al. Nanocarbons from rice husk by microwave plasma irradiation: from graphene and carbon nanotubes to graphenated carbon nanotube hybrids. Carbon 2015;94:479–84.

[33] Bernd MGS, Bragança SR, Heck N, Filho LCPDS. Synthesis of carbon nanostructures by the pyrolysis of wood sawdust in a tubular reactor. J Mater Res Technol 2017;6:171–7.

[34] Yan Q, Li J, Zhang X, Hassan EB, Wang C, Zhang J, Cai Z. Catalytic graphitization of kraft lignin to graphene-based structures with four different transitional metals. J Nanopart Res 2018;20:223.

[35] Köhnke J, Fürst C, Unterweger C, Rennhofer H, Lichtenegger HC, Keckes J, Emsenhuber G, Mahendran A, Liebner F, Gindl-Altmutter W. Carbon microparticles from organosolv lignin as filler for conducting Poly(lactic acid). Polymers 2016;8:205.

[36] Andrews R, Jacques D, Qian D, Rantell T. Multiwall carbon nanotubes: synthesis and application. Accounts Chem Res 2002;35:1008–17.

[37] Dai HJ. Carbon nanotubes: synthesis, integration, and properties. Accounts Chem Res 2002;35:1035–44.

[38] Kumar M, Ando Y. Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production. J Nanosci Nanotechnol 2010;10:3739–58.

[39] Reibold M, Paufler P, Levin AA, Kochmann W, Pätzke N, Meyer DC. Carbon nanotubes in an ancient Damascus sabre. Nature 2006;444:286.