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(54) **METHOD TO PRODUCE HIGH-QUALITY CARBON FIBER USING LIGNIN**

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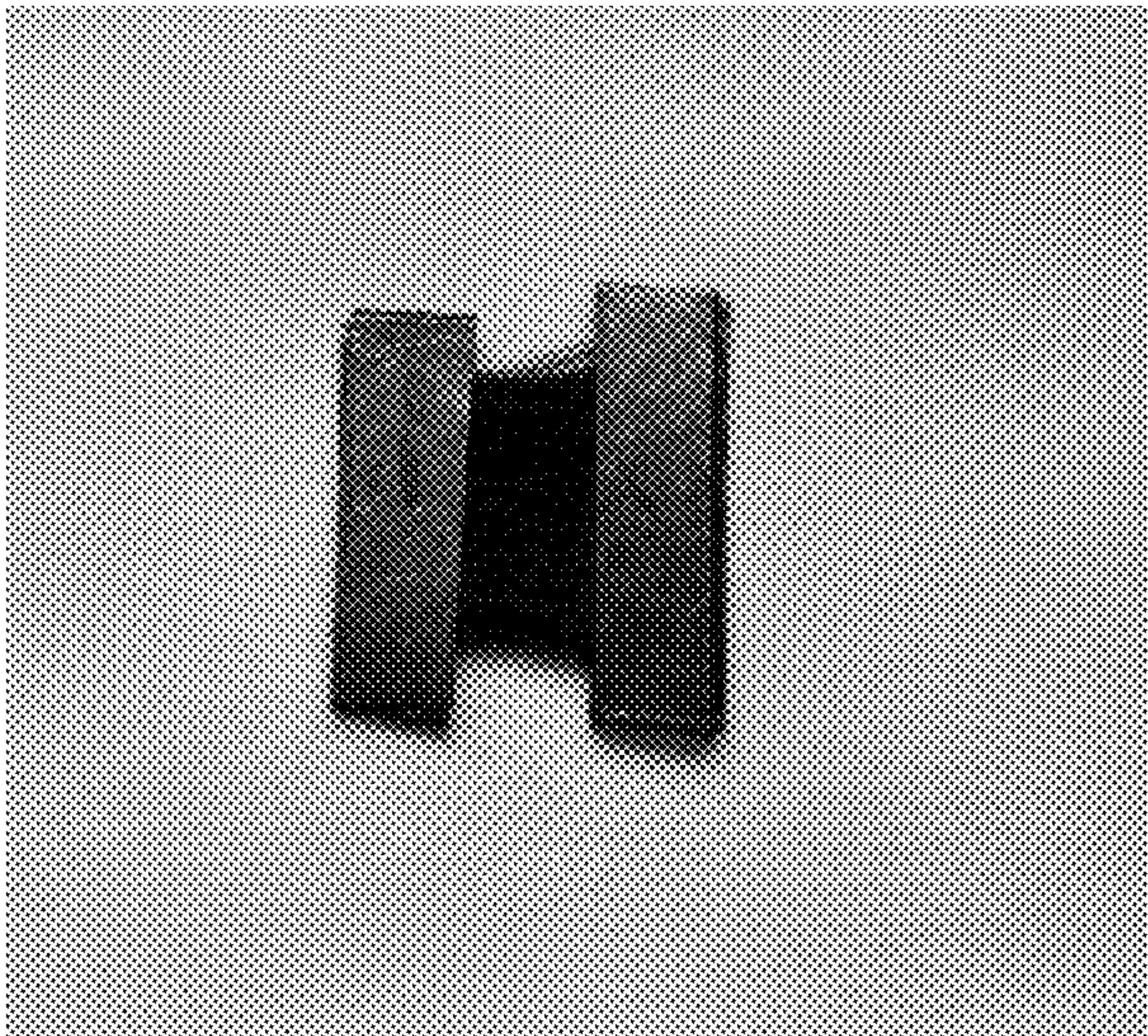
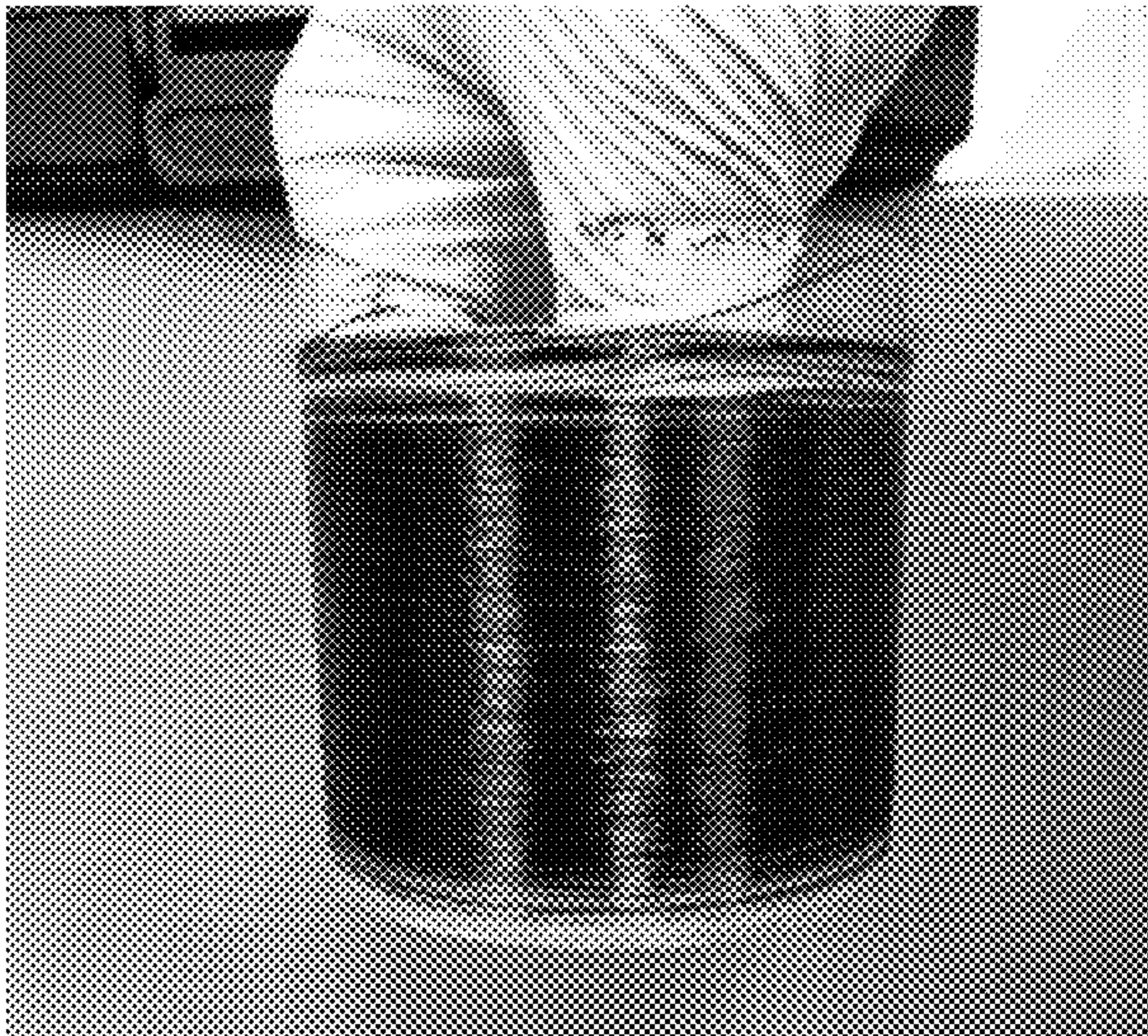
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CPC **D01F 9/17** (2013.01); **D10B 2101/12** (2013.01); **D10B 2401/063** (2013.01); **D10B 2401/10** (2013.01); **D10B 2505/12** (2013.01)

(57) **ABSTRACT**

The present application is directed to a method of producing a lignin-based carbon fiber. This method comprises providing a lignin-containing material; producing a lignin fiber from the lignin-containing material; stabilizing the lignin fiber under tension, where the tension is adjusted during said stabilizing such that the maximum bearable tension is applied to the lignin fiber; and carbonizing the lignin fiber under tension to produce a carbon fiber, where said carbonizing is carried out at a temperature below 1200° C. and where the tension during said carbonizing is adjusted to avoid shrinkage. The present application is also directed to a lignin-based carbon fiber and molded articles containing such fibers.



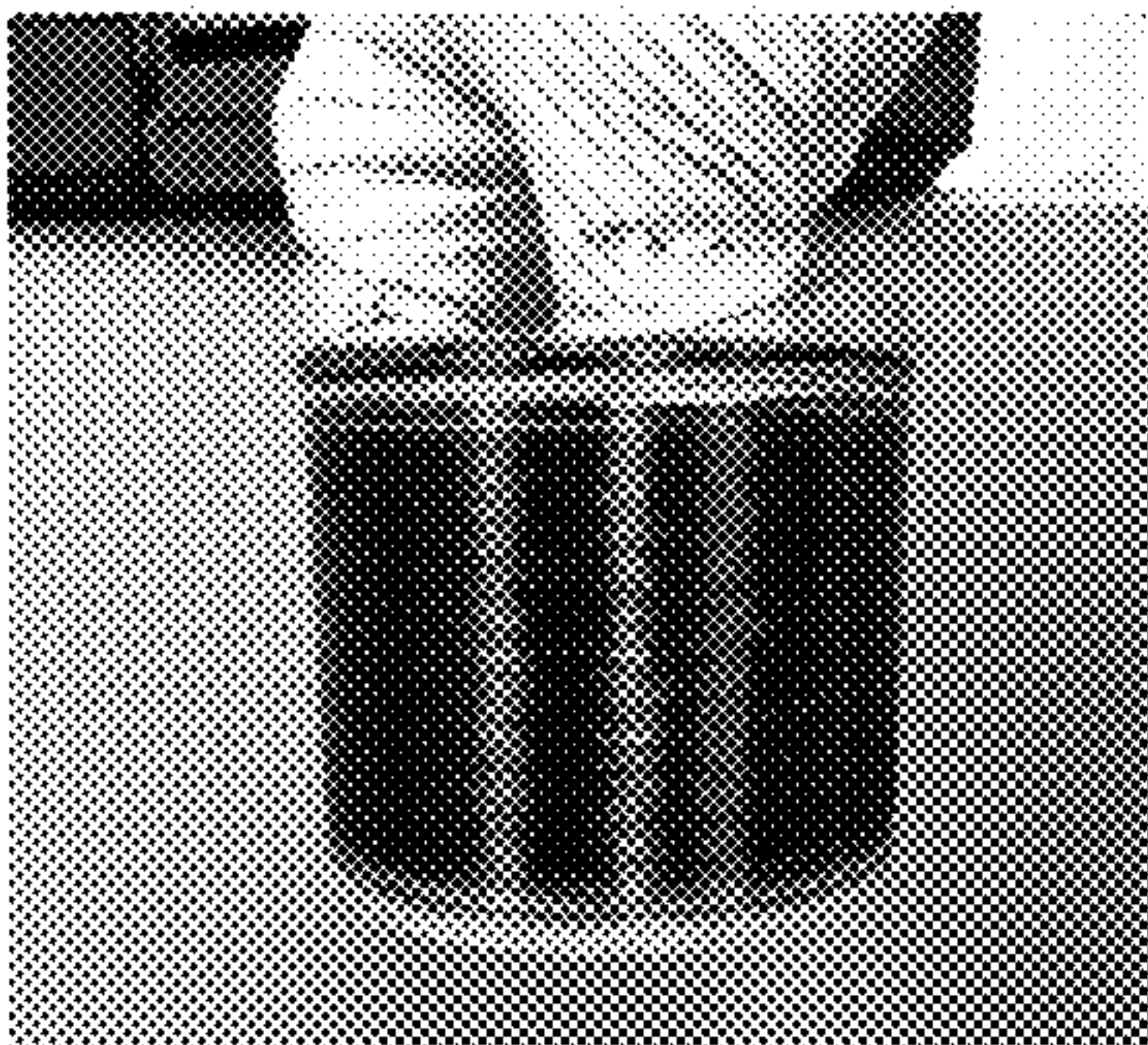


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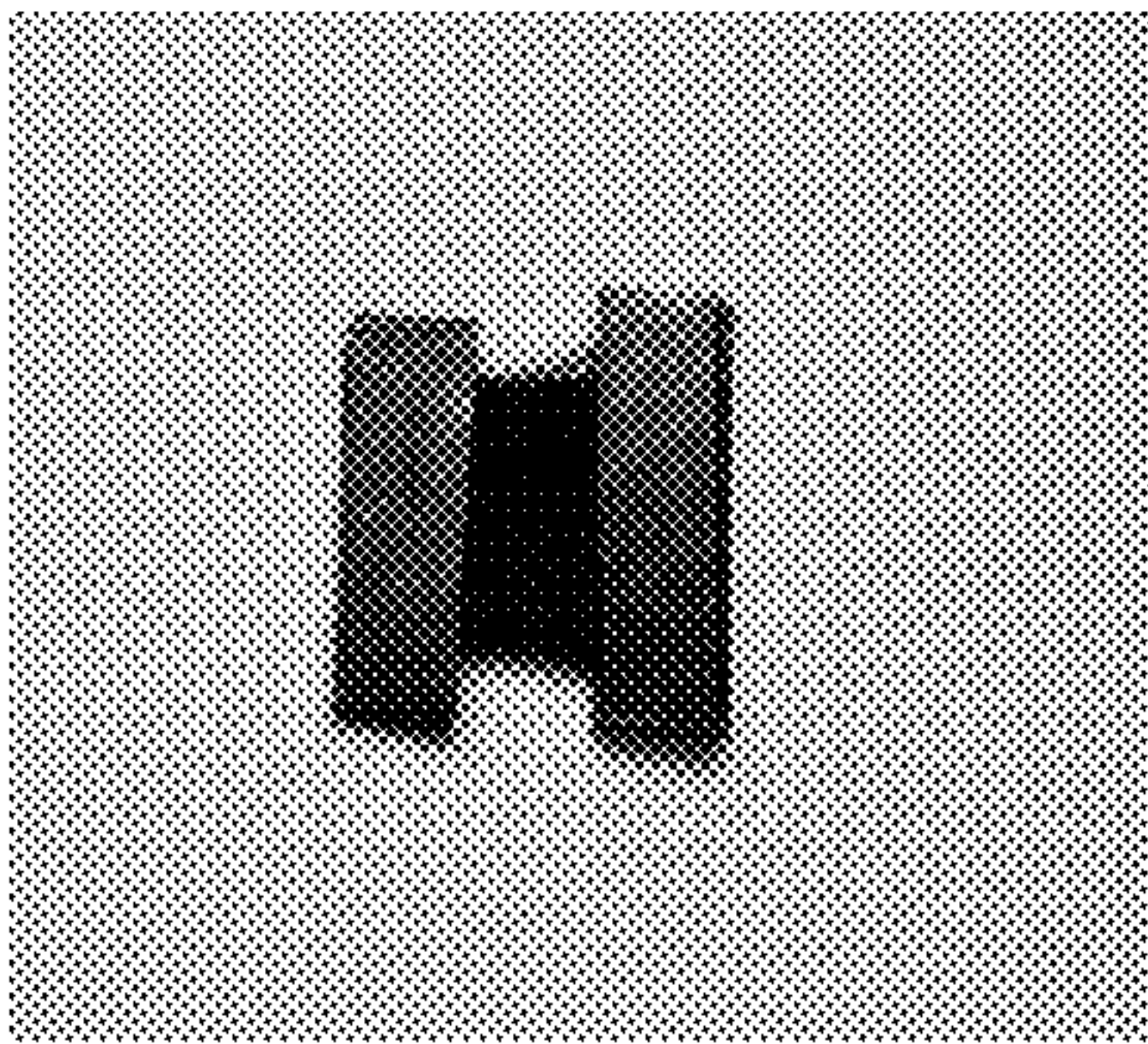


Figure 1B

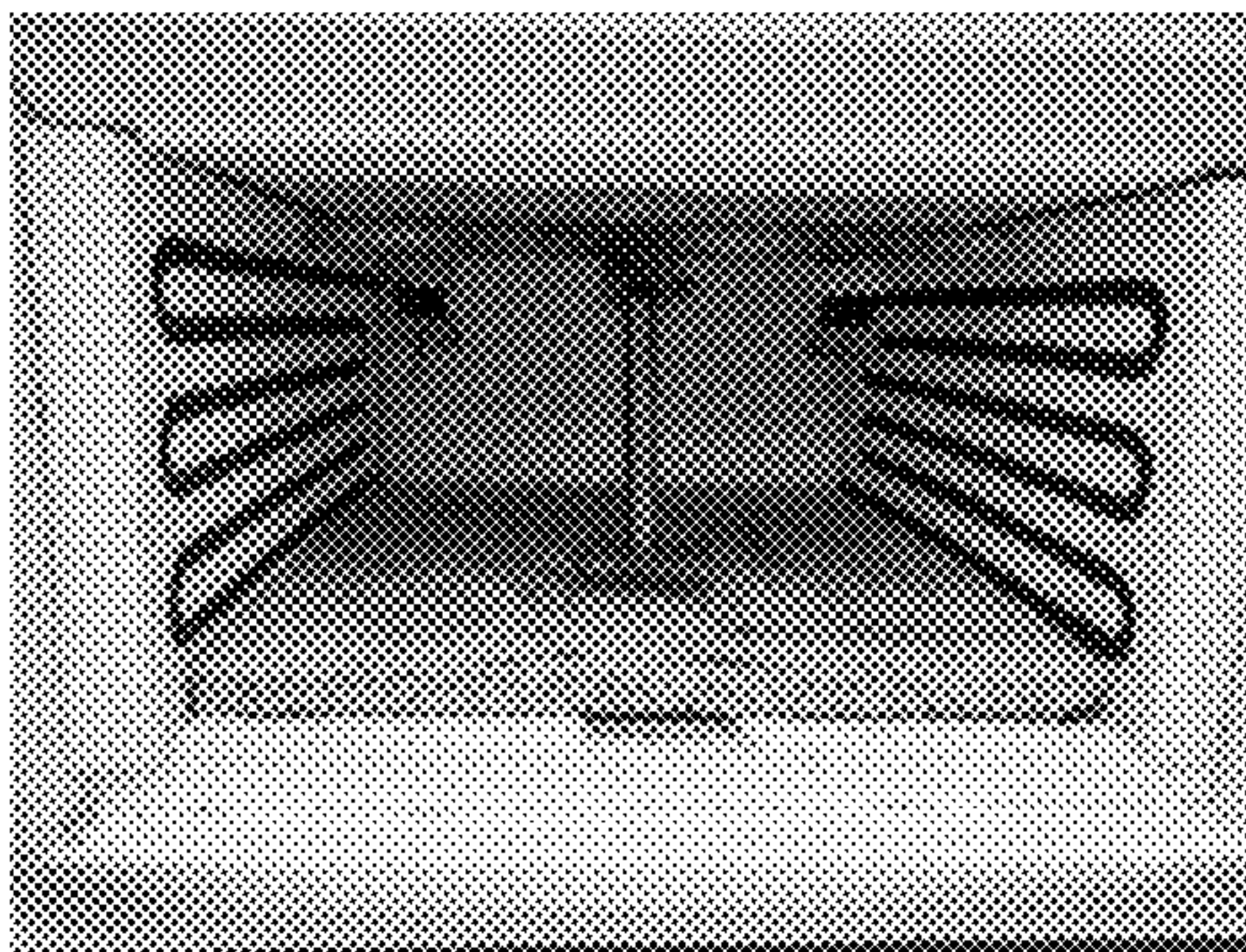


Figure 1C

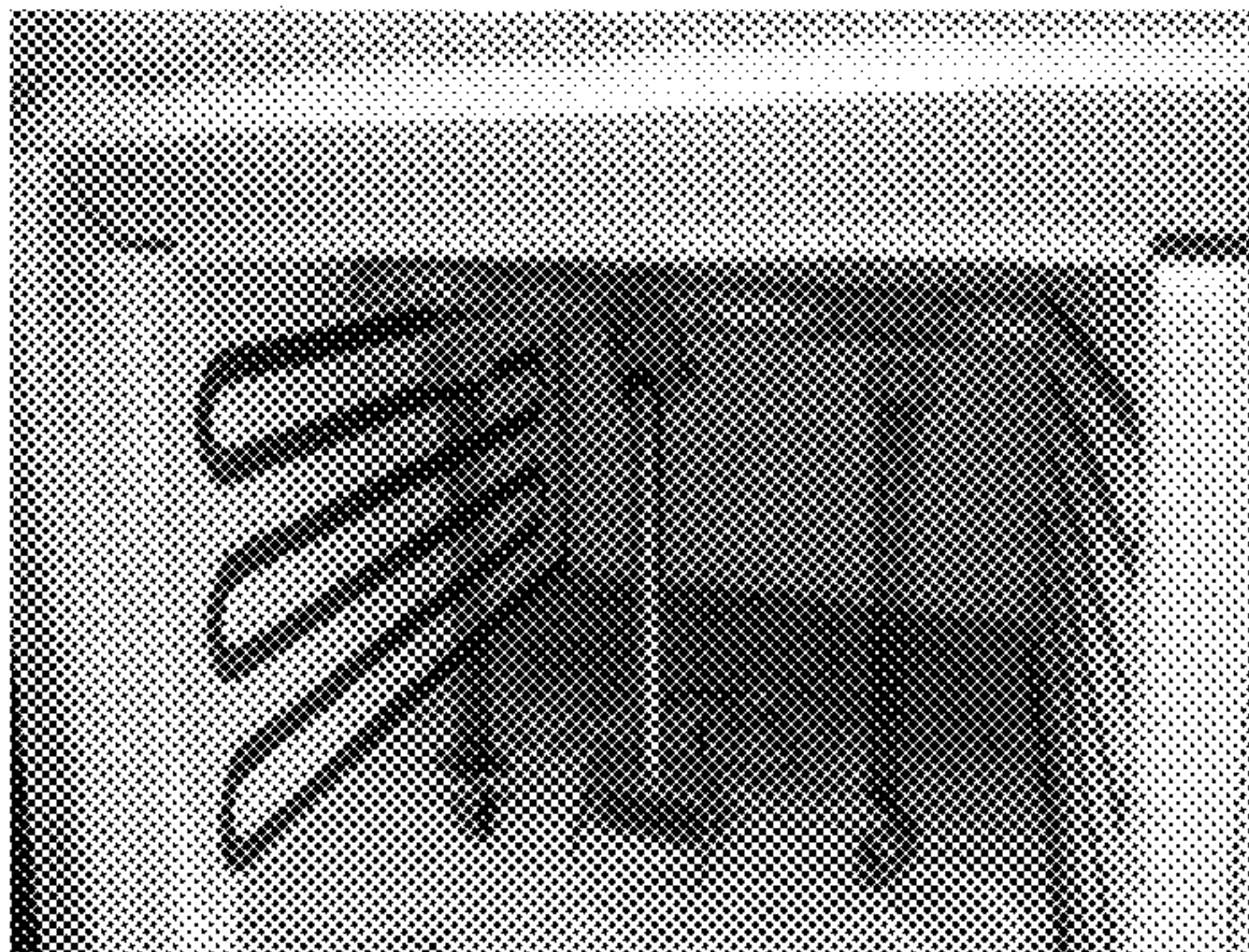


Figure 1D

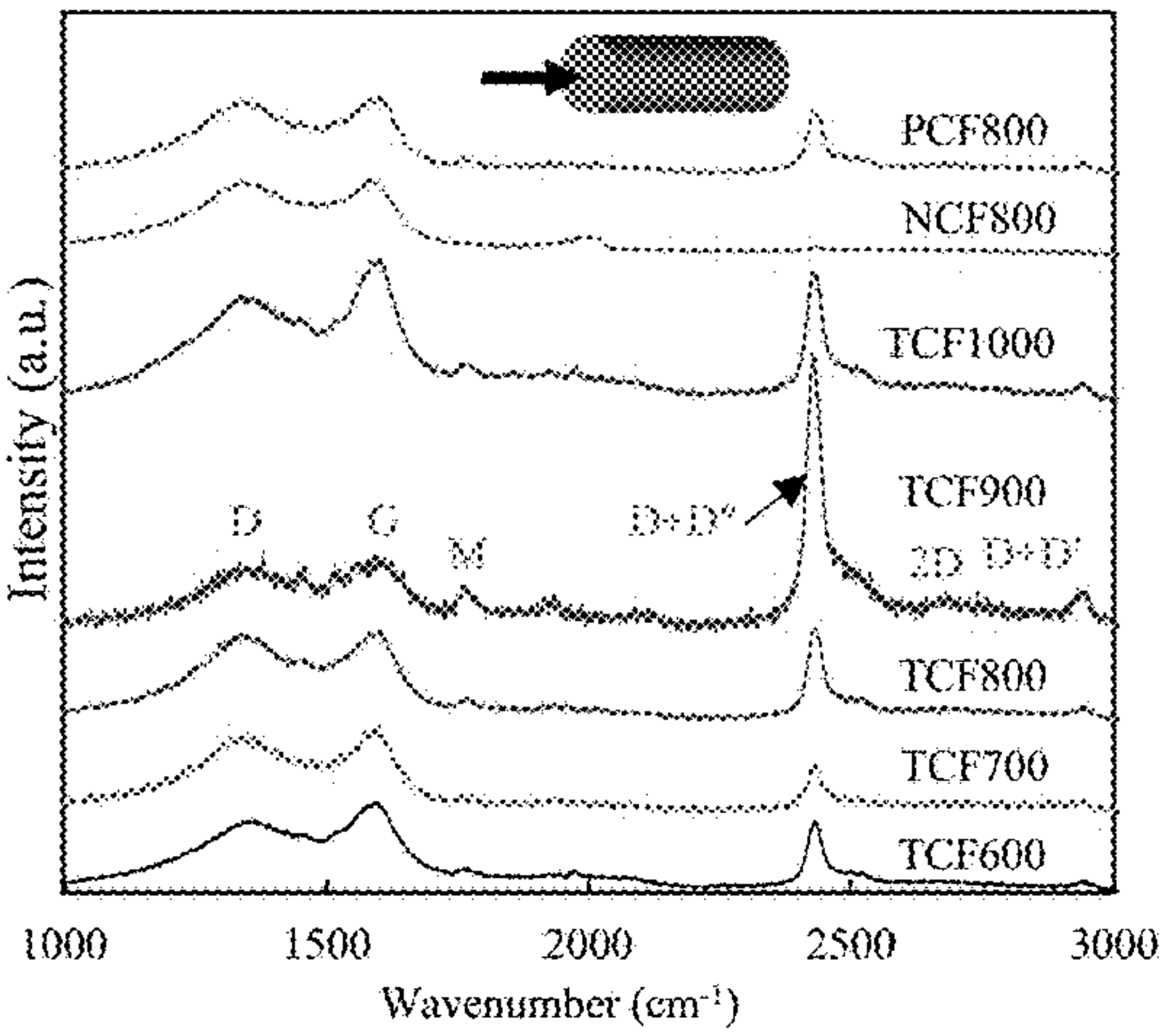


Figure 2A

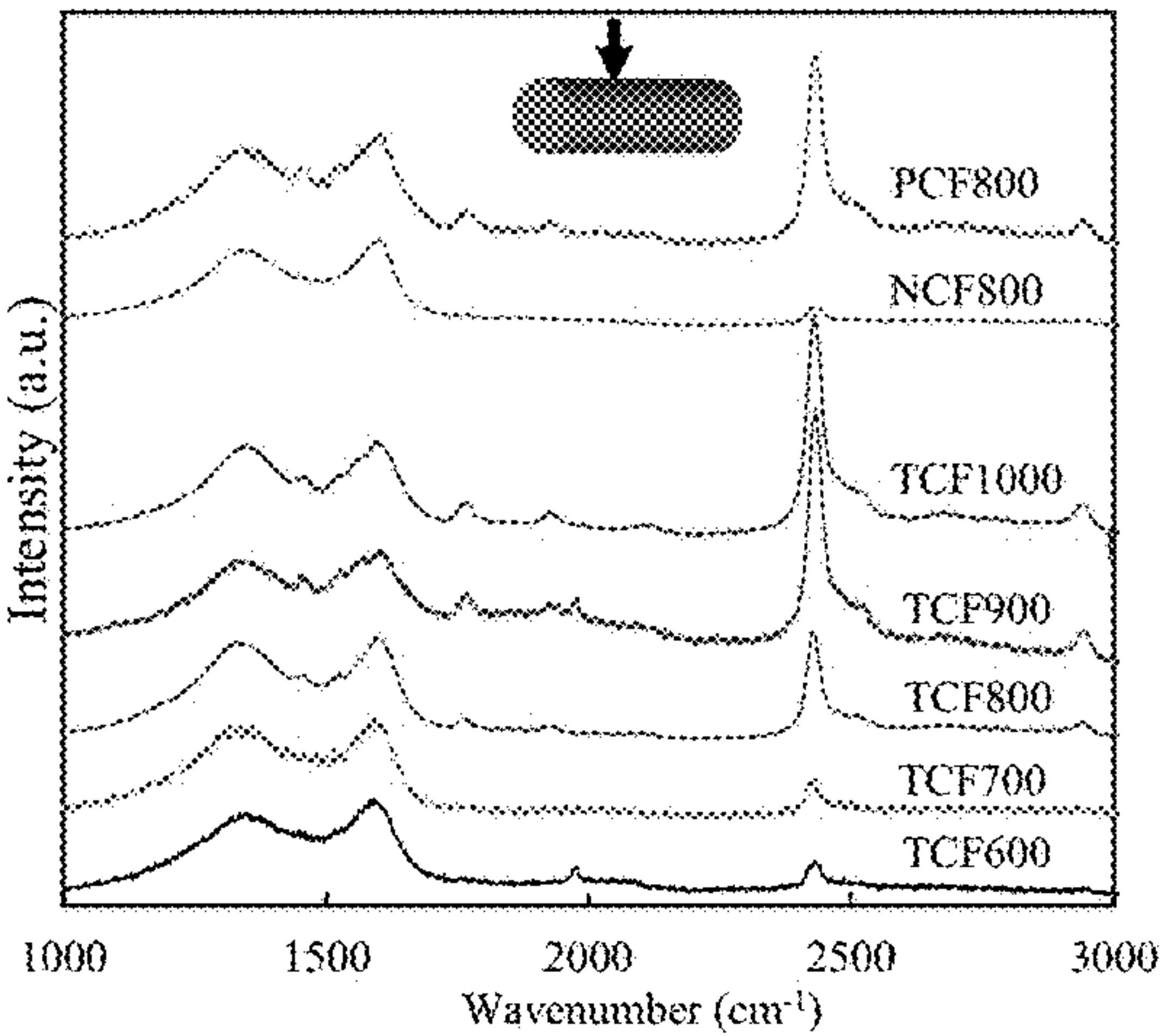


Figure 2B

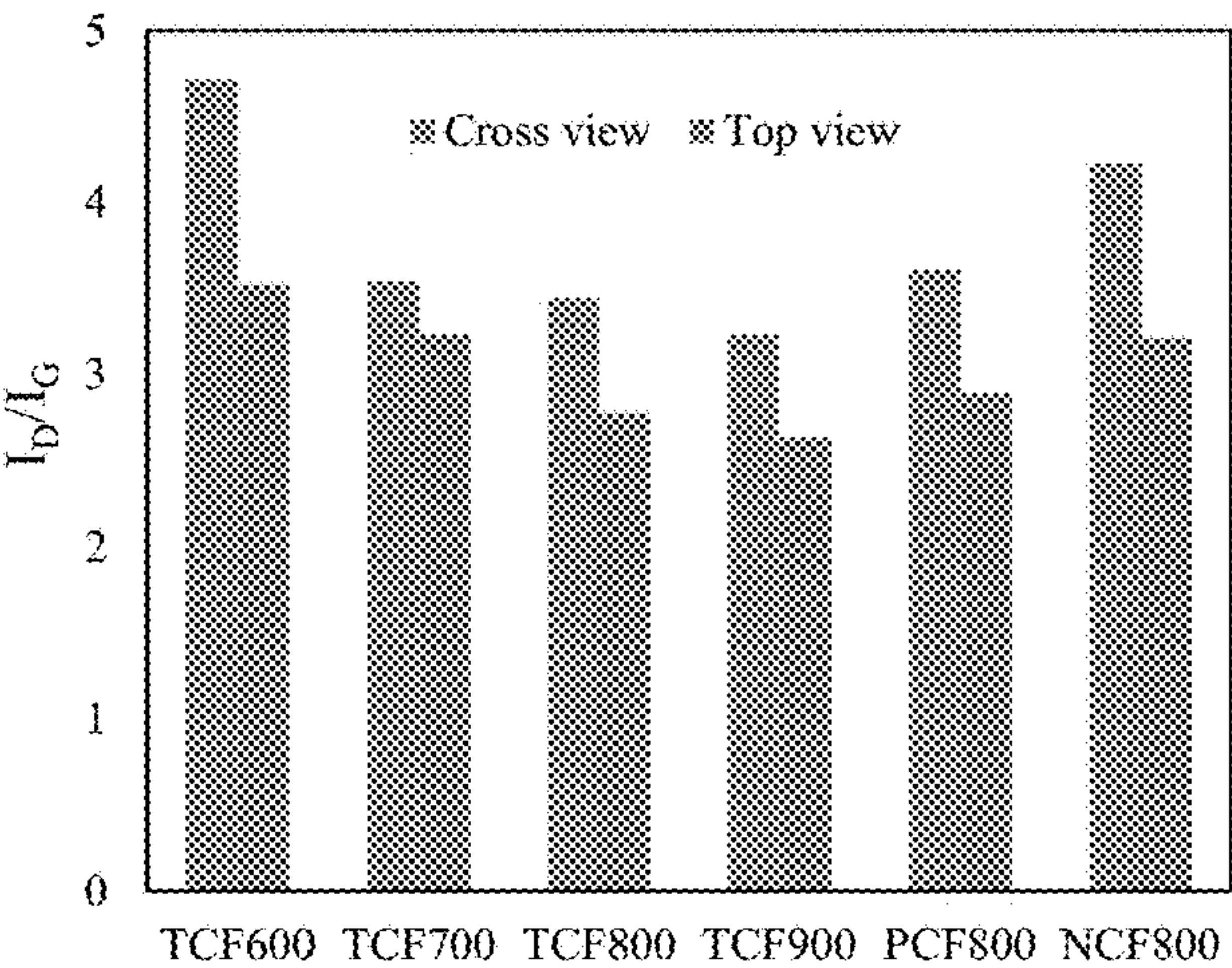


Figure 2C

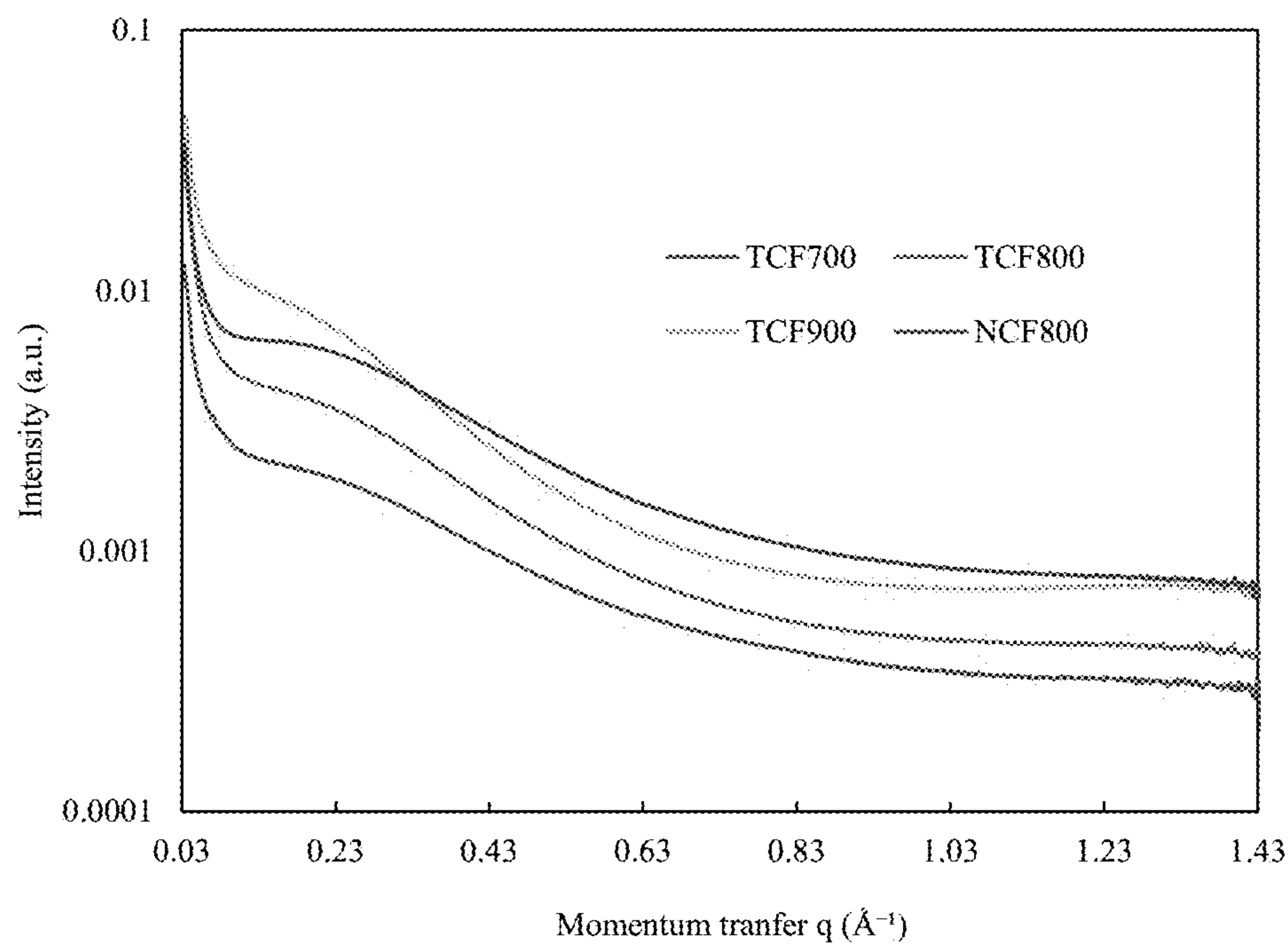


Figure 3

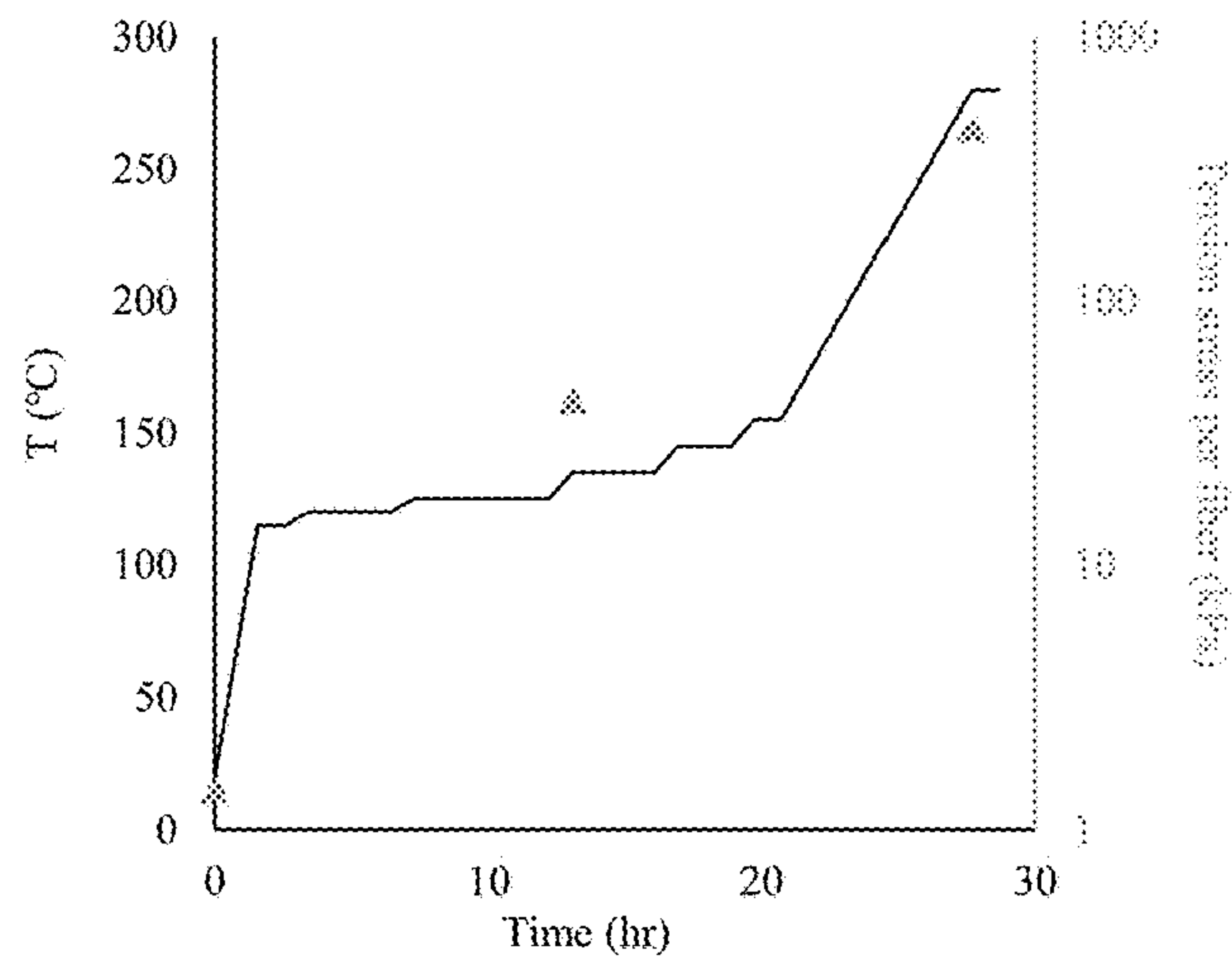


Figure 4A

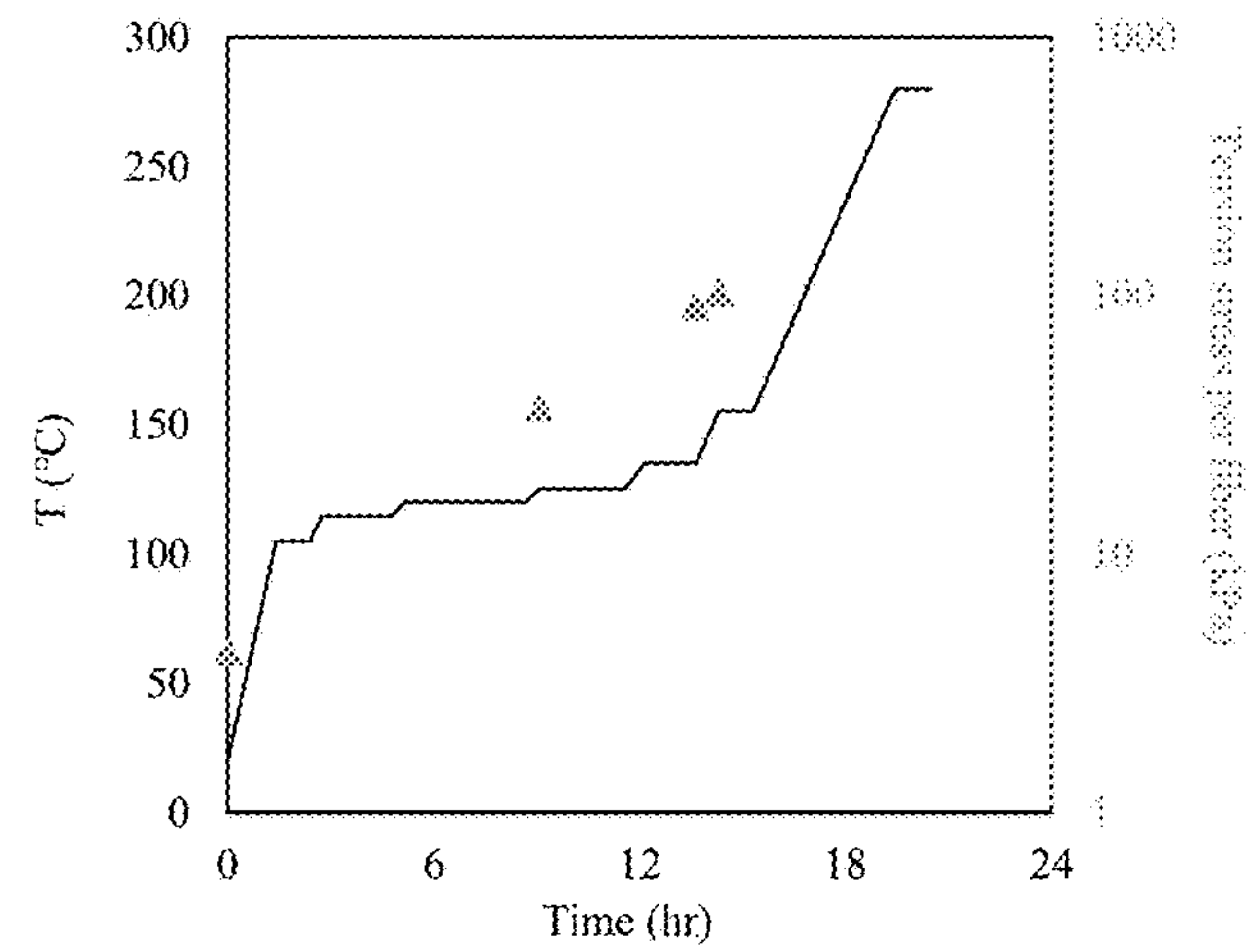


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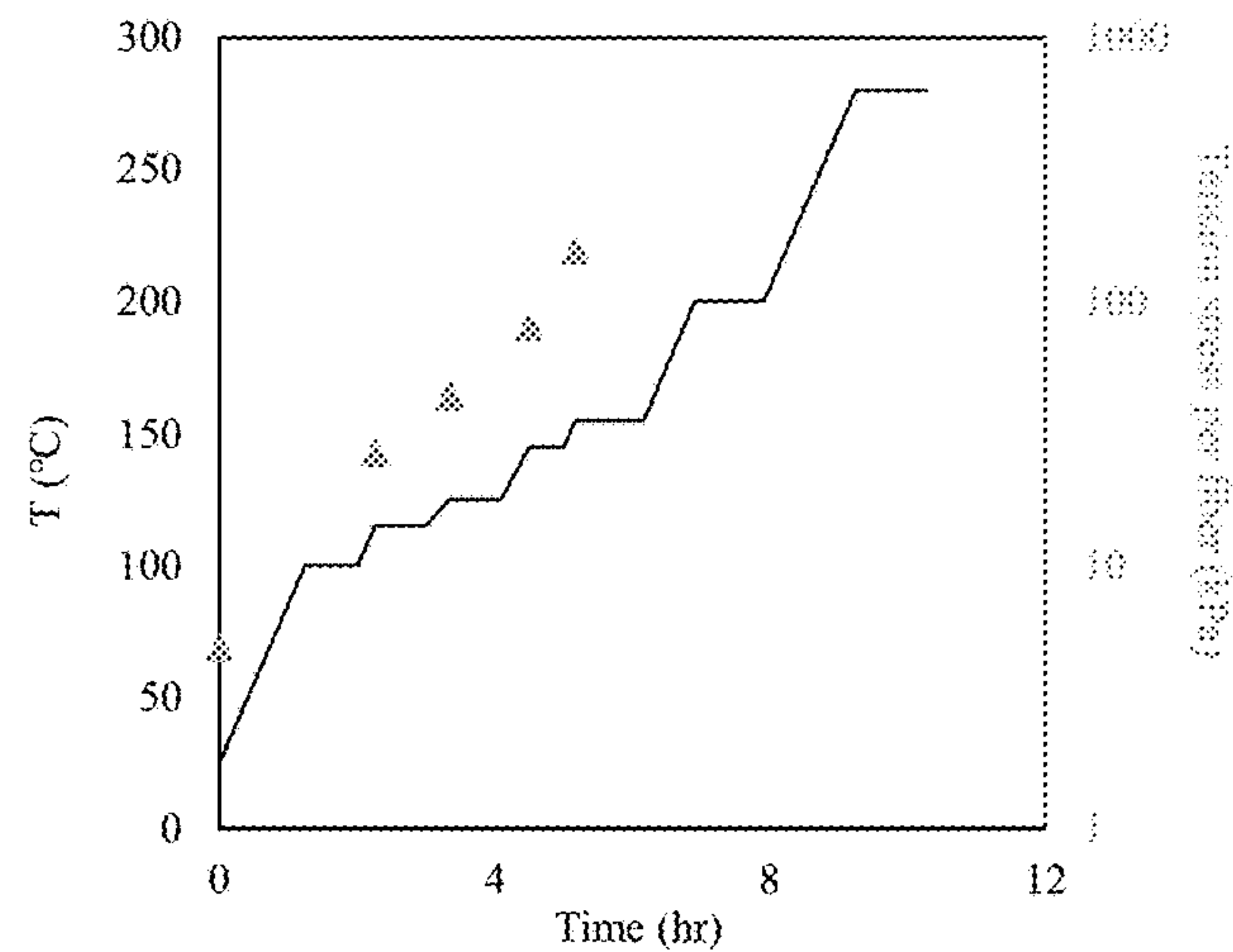


Figure 4C

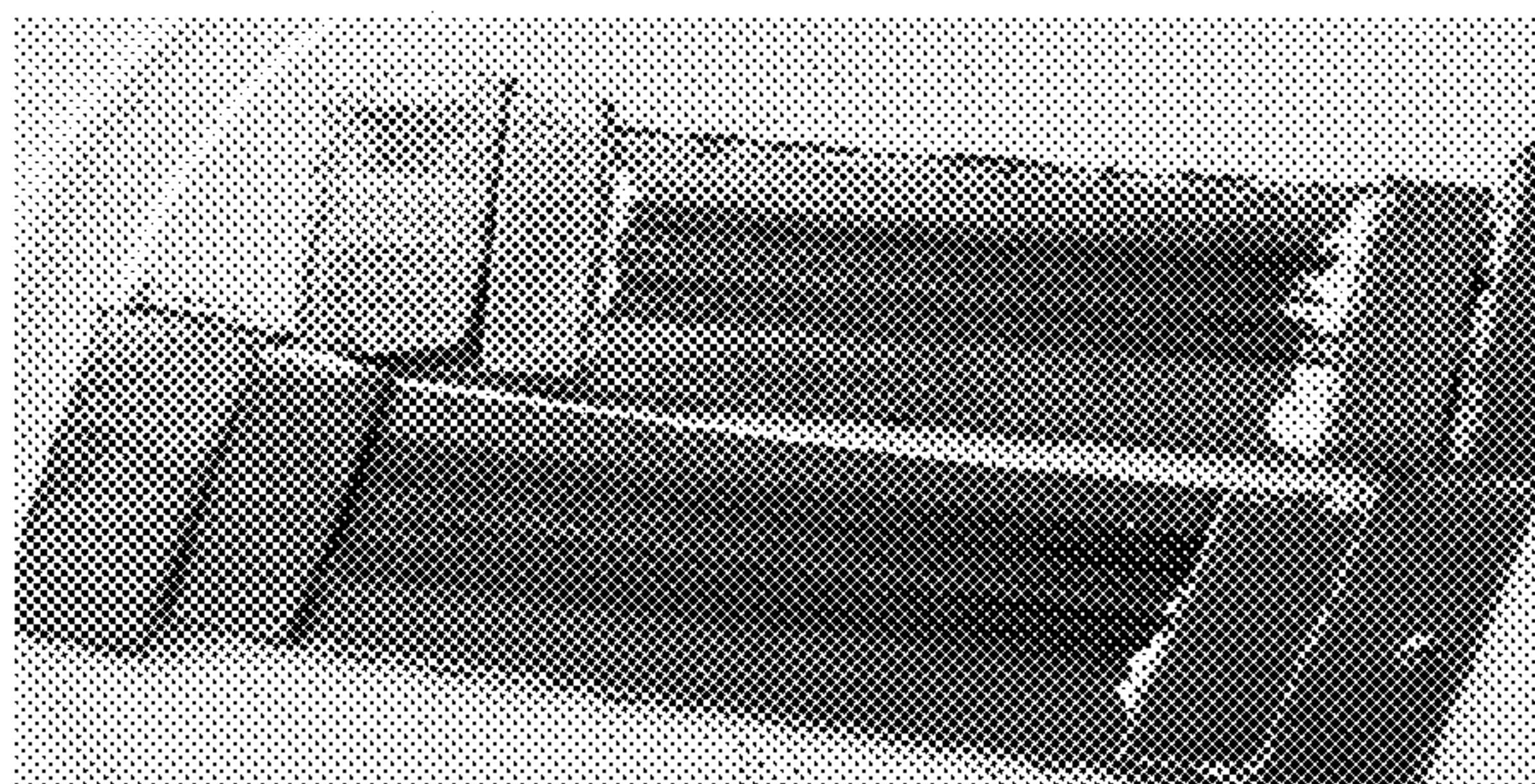


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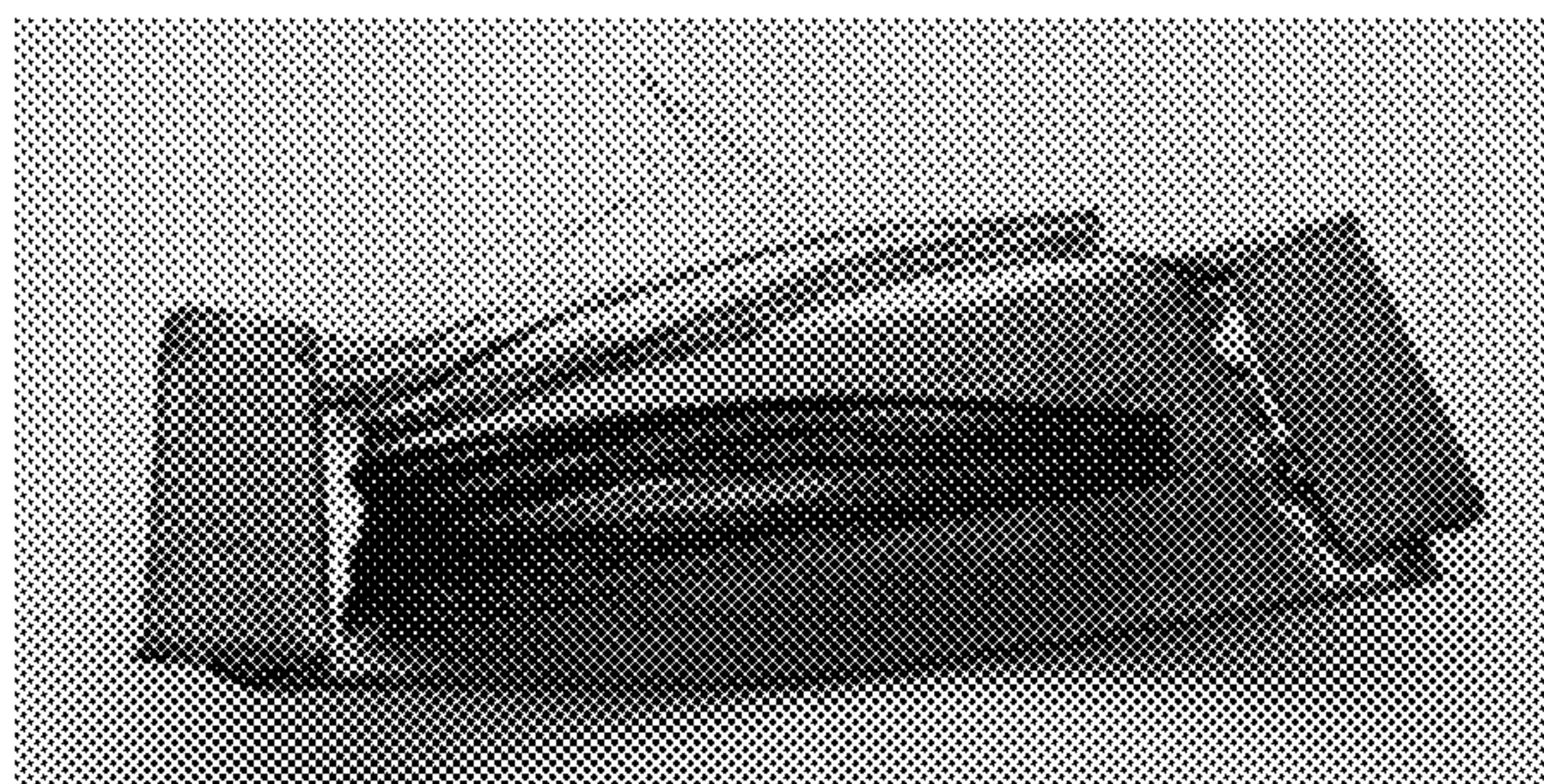


Figure 5B

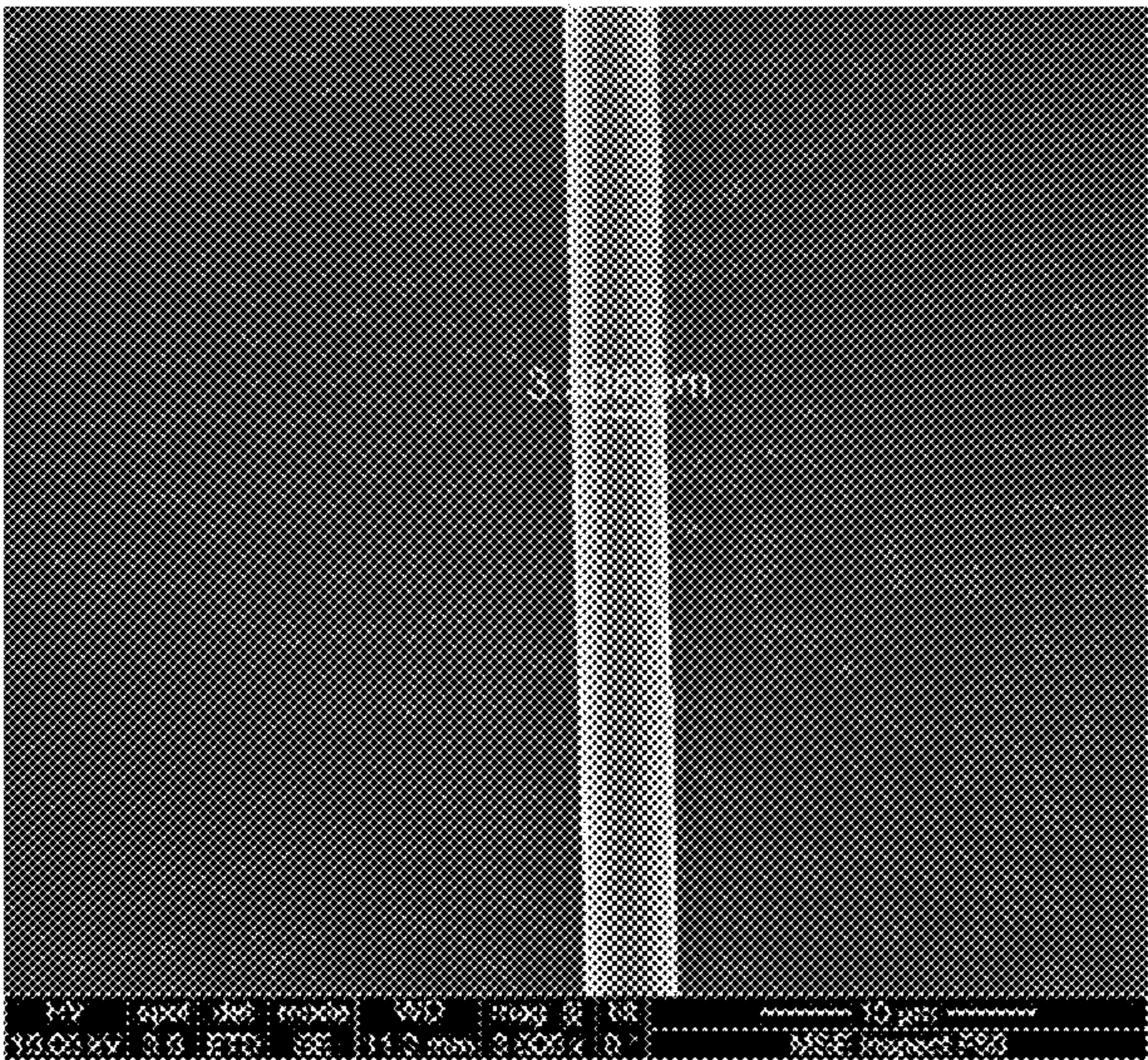


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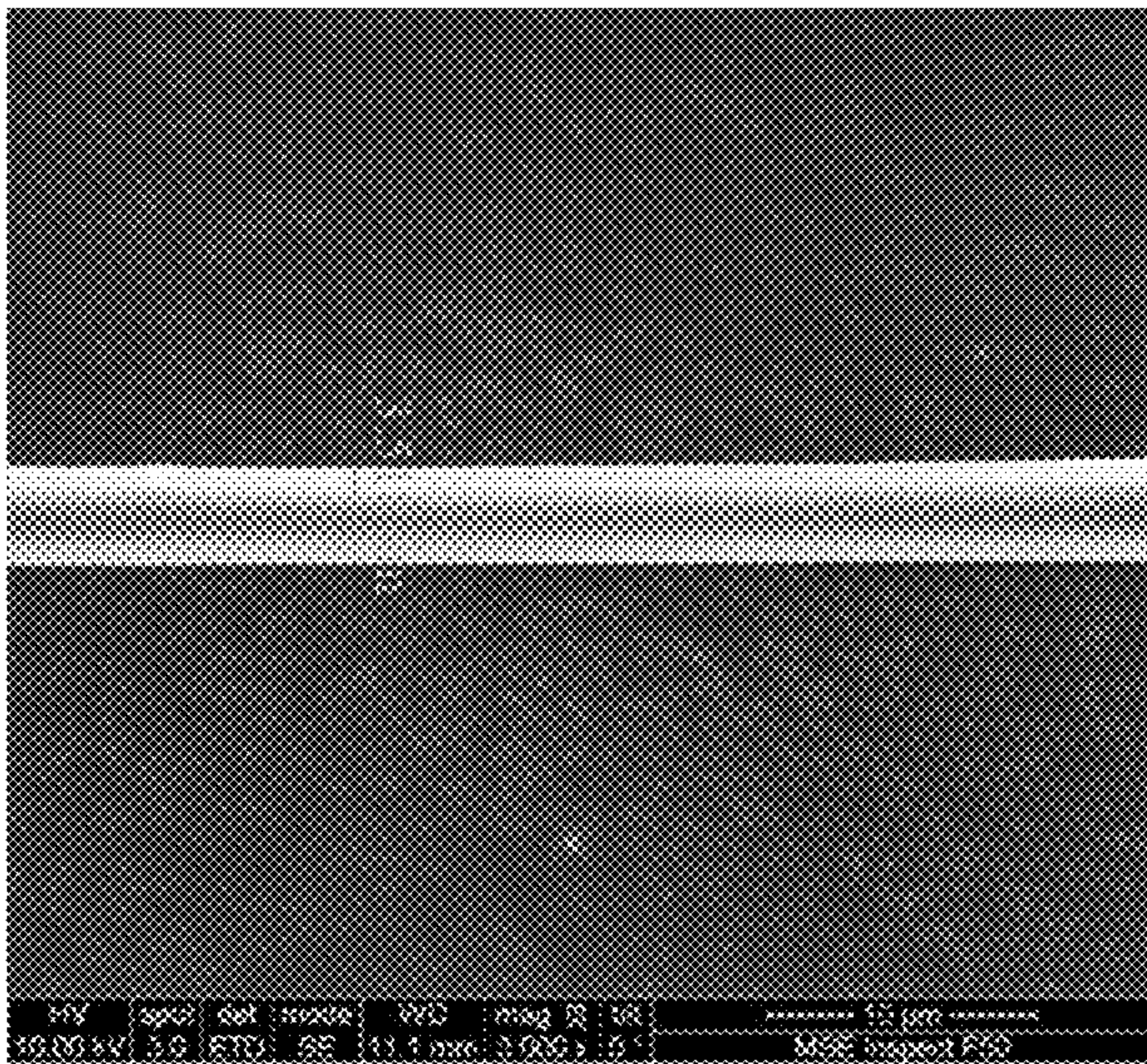


Figure 6B

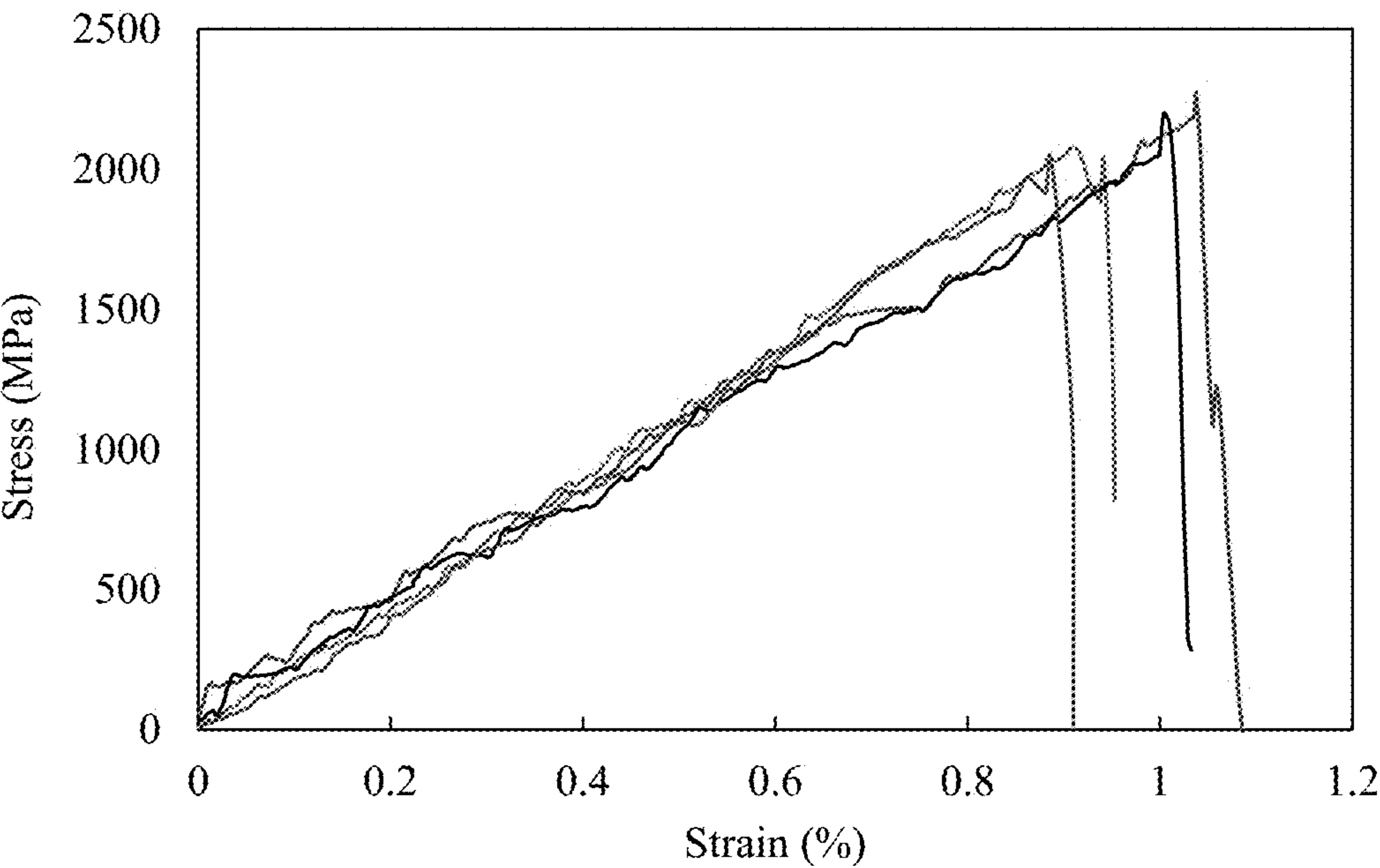


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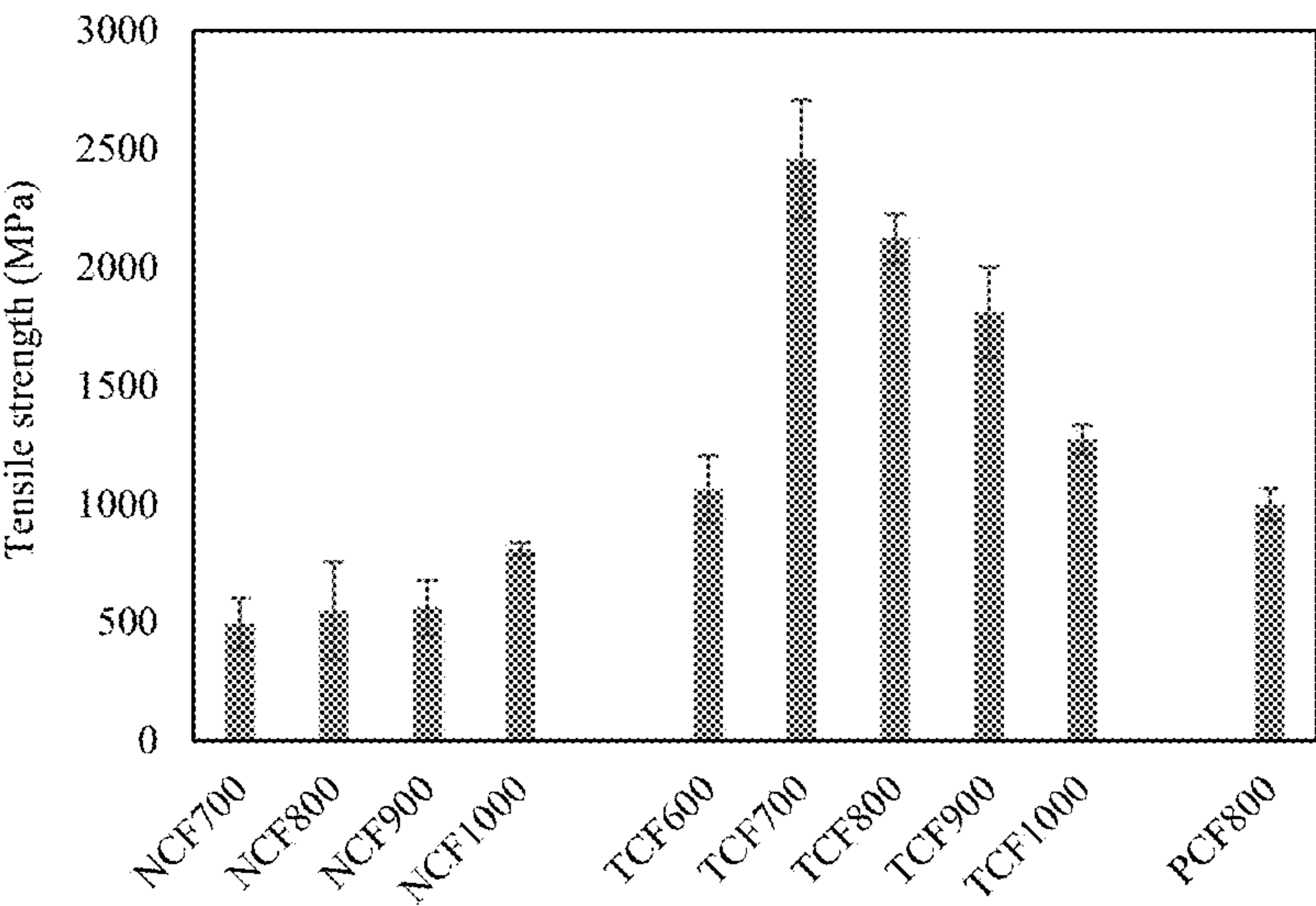


Figure 8A

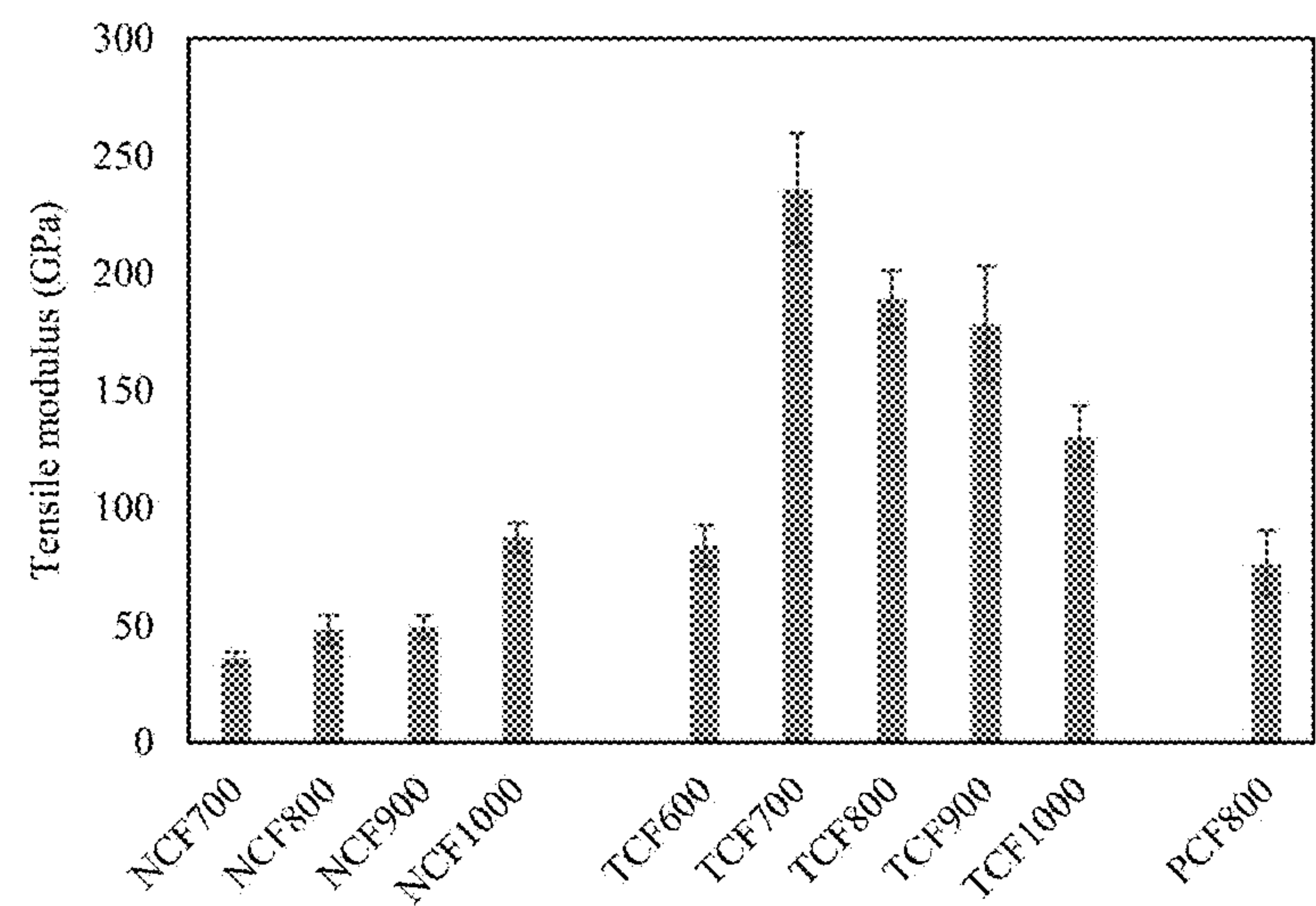


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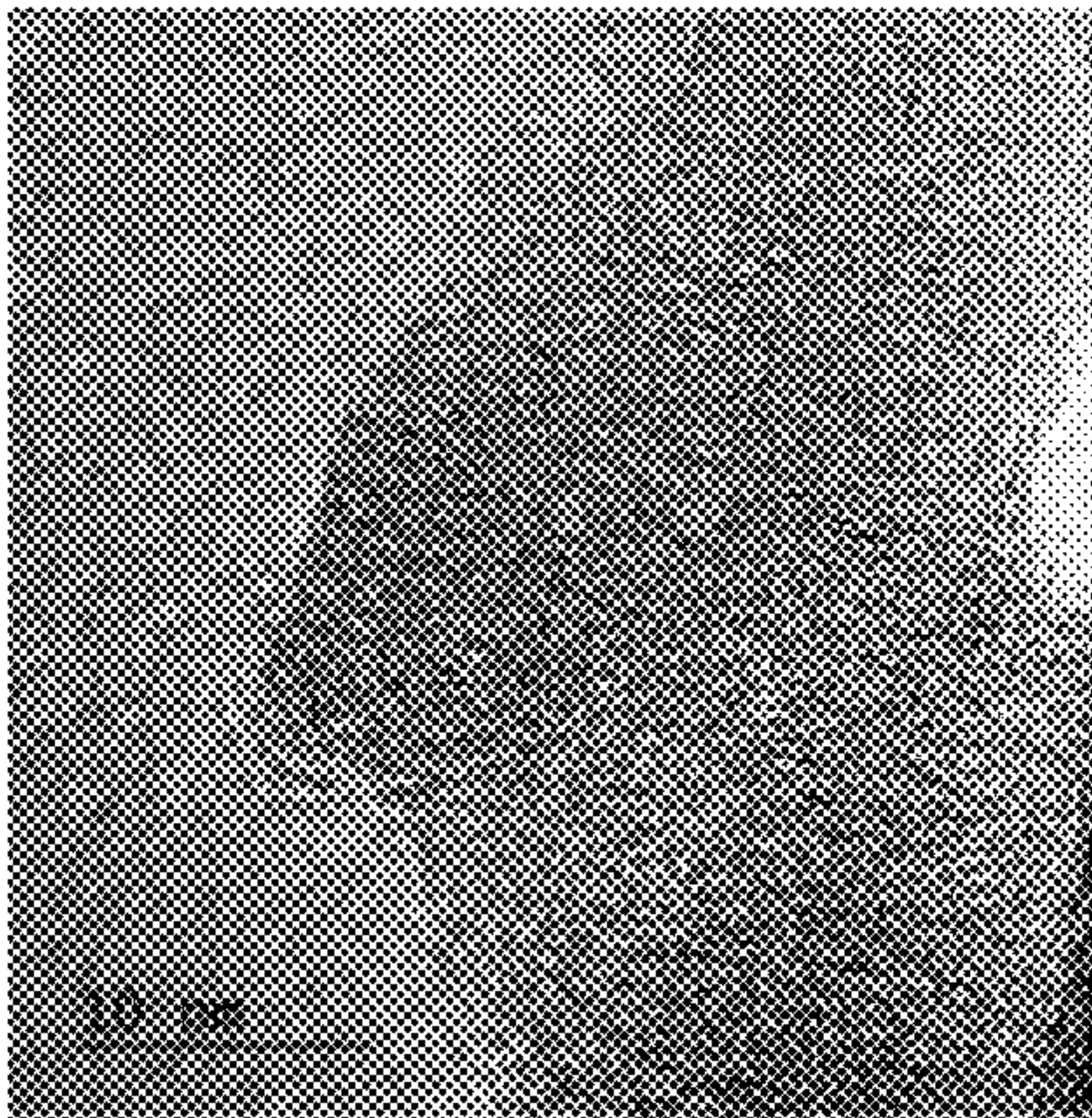


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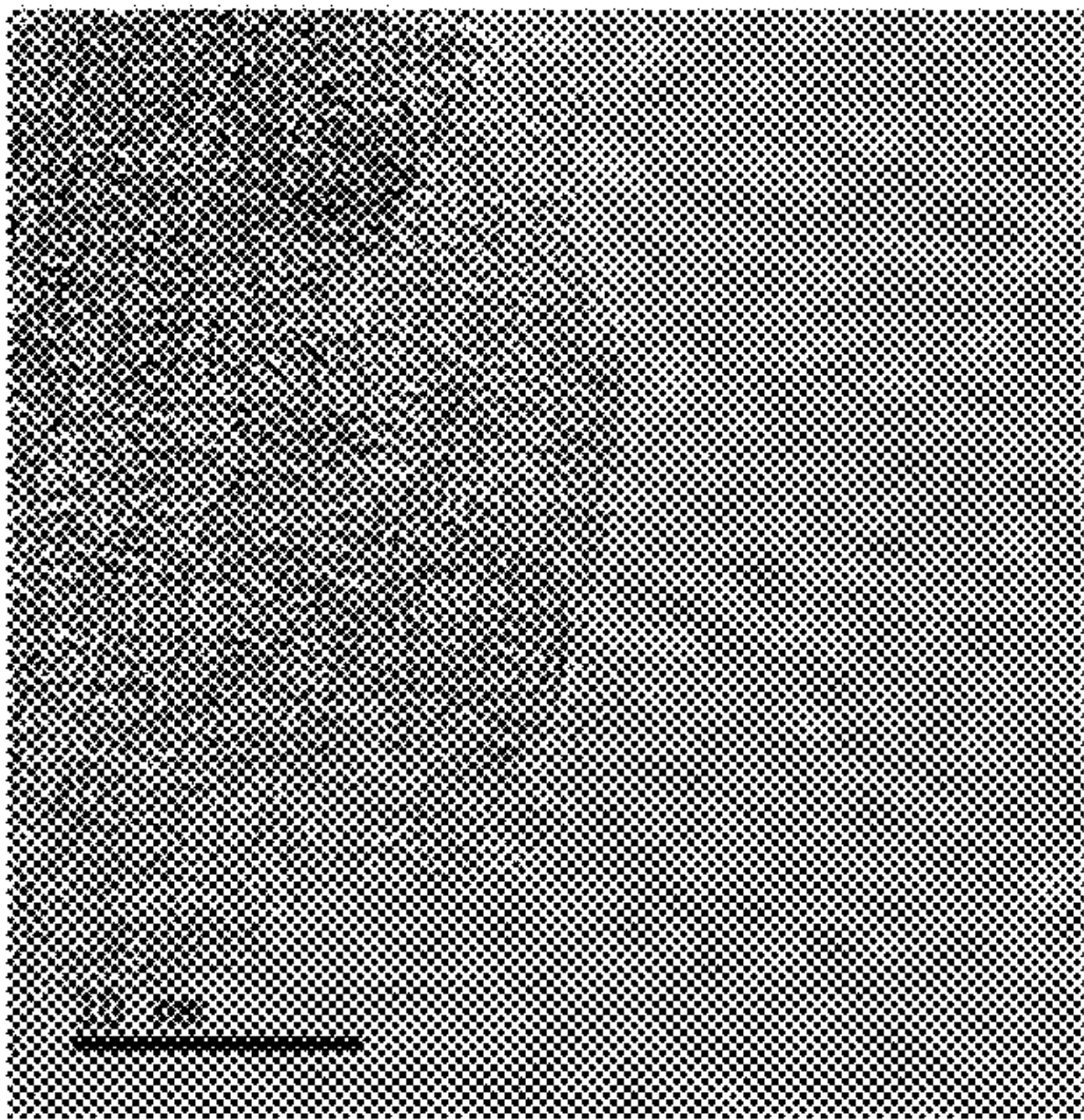


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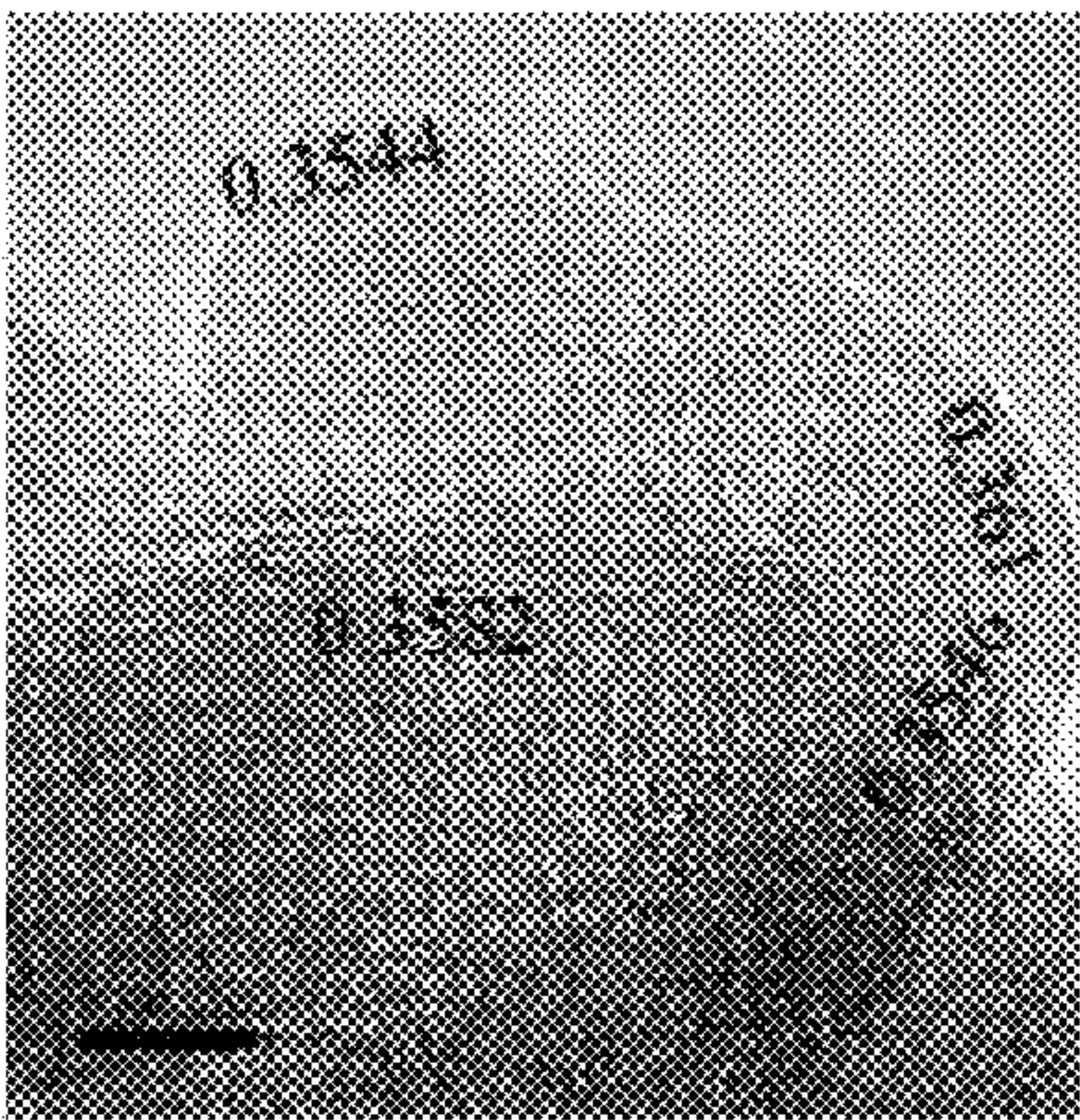


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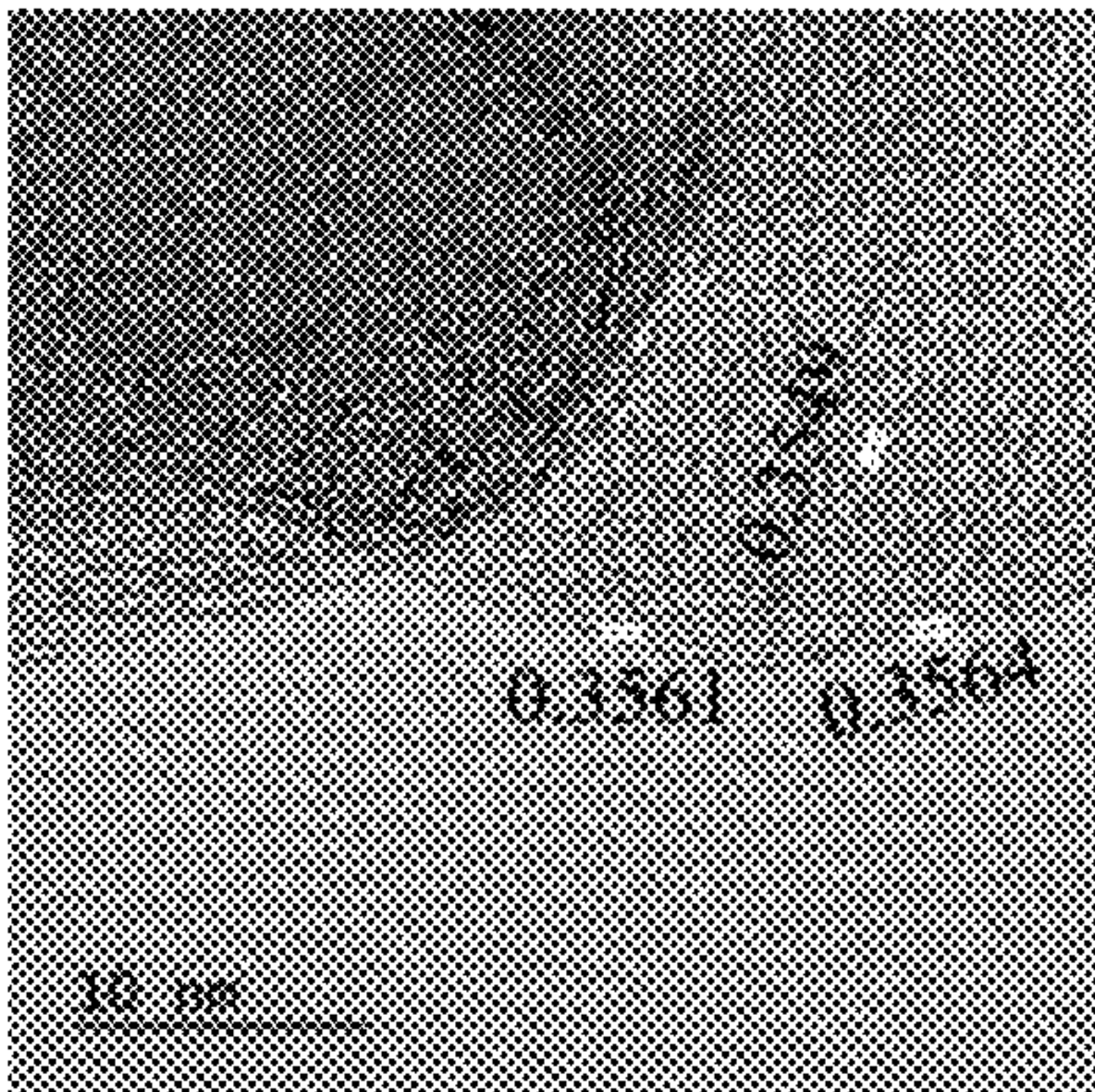


Figure 9D

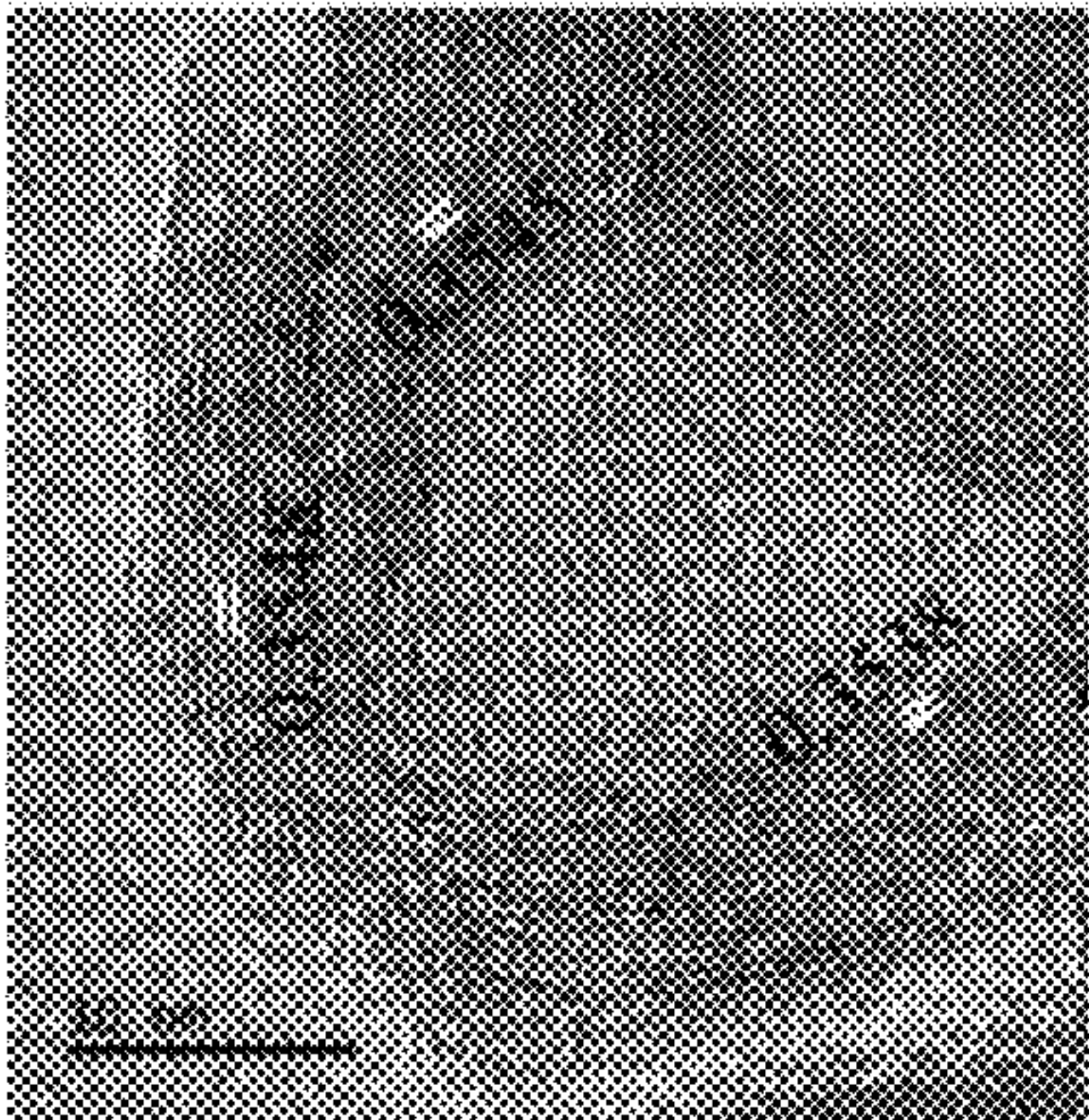


Figure 9E

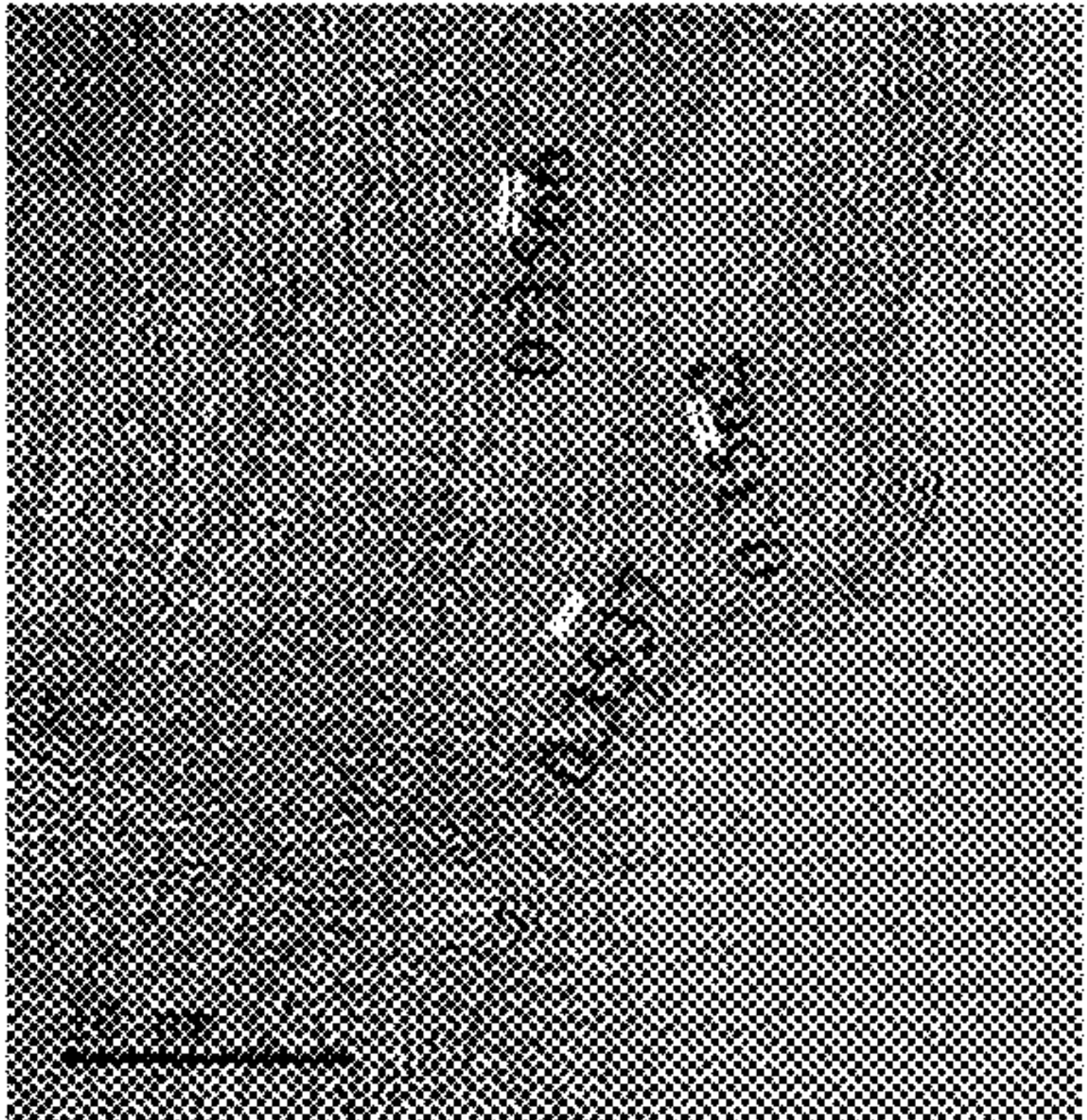


Figure 9F

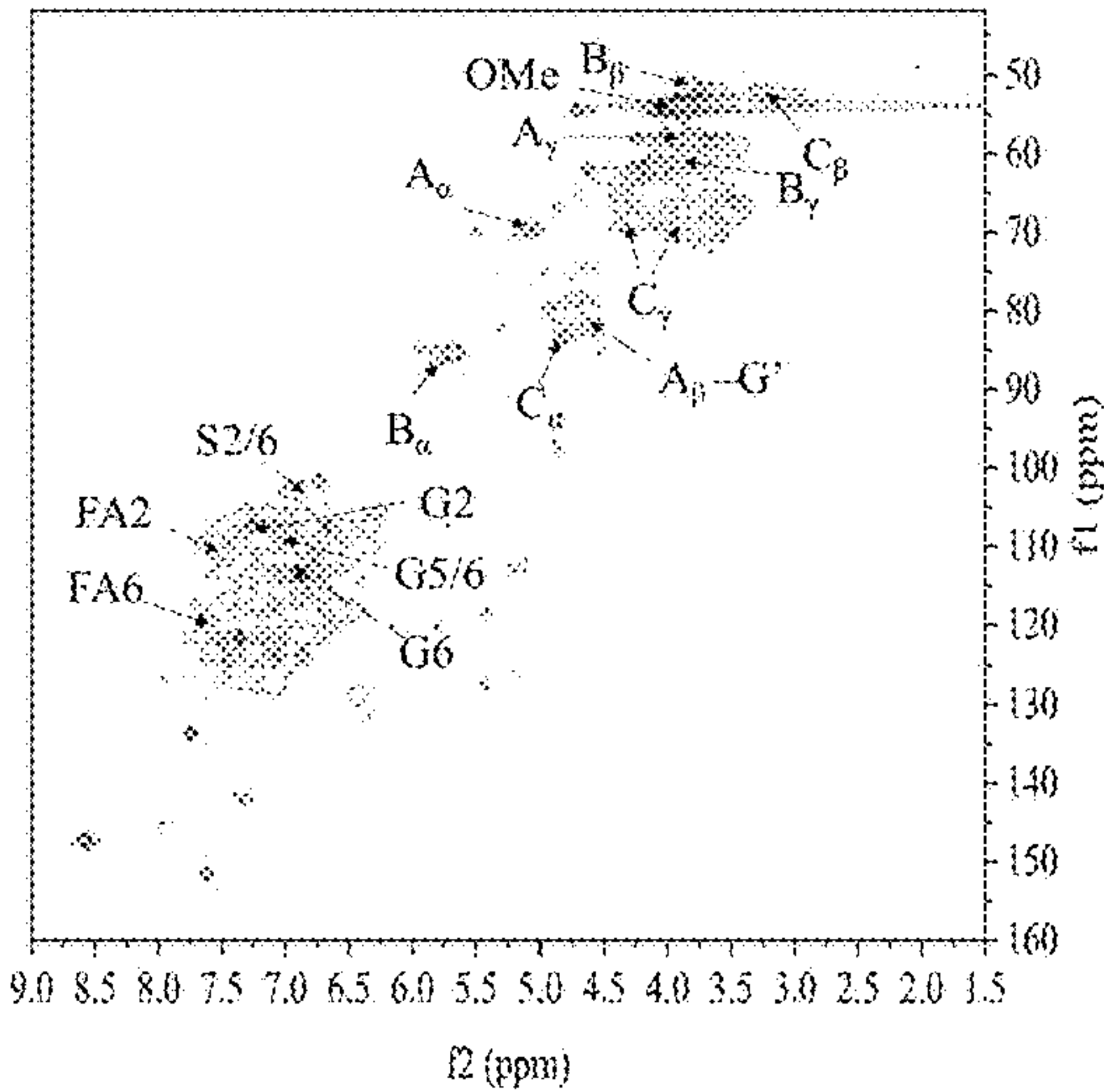


Figure 10A

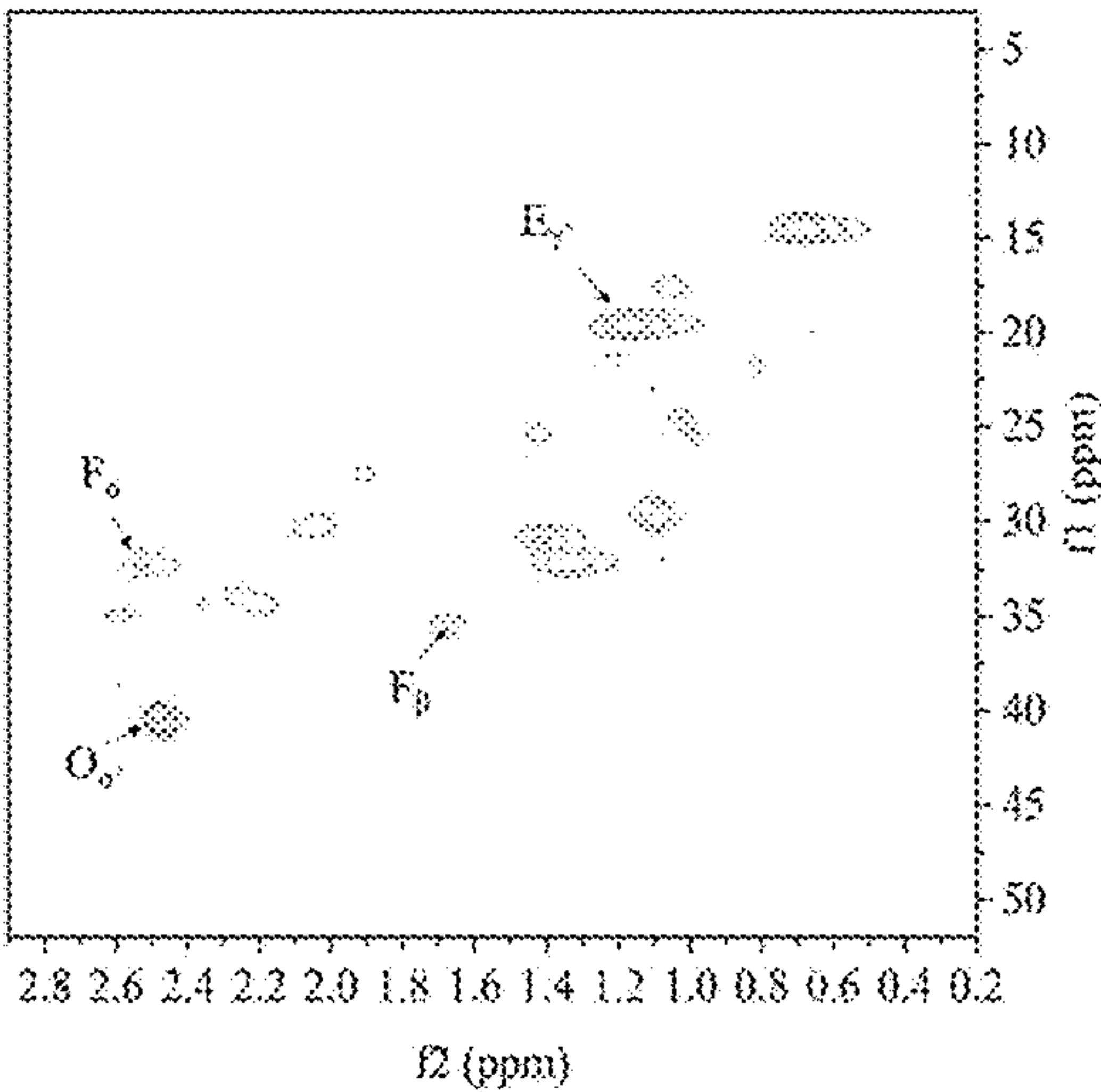


Figure 10B

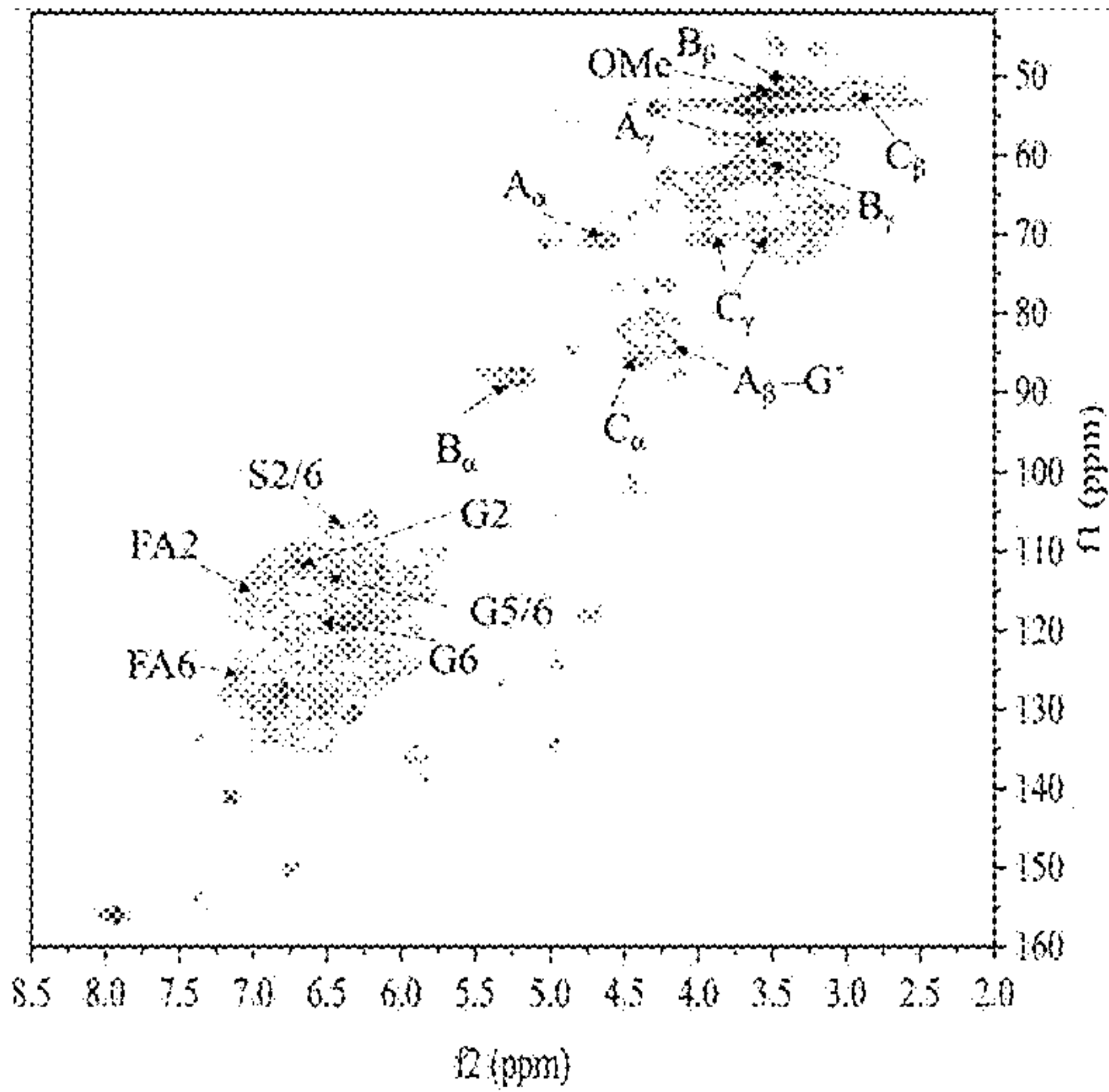


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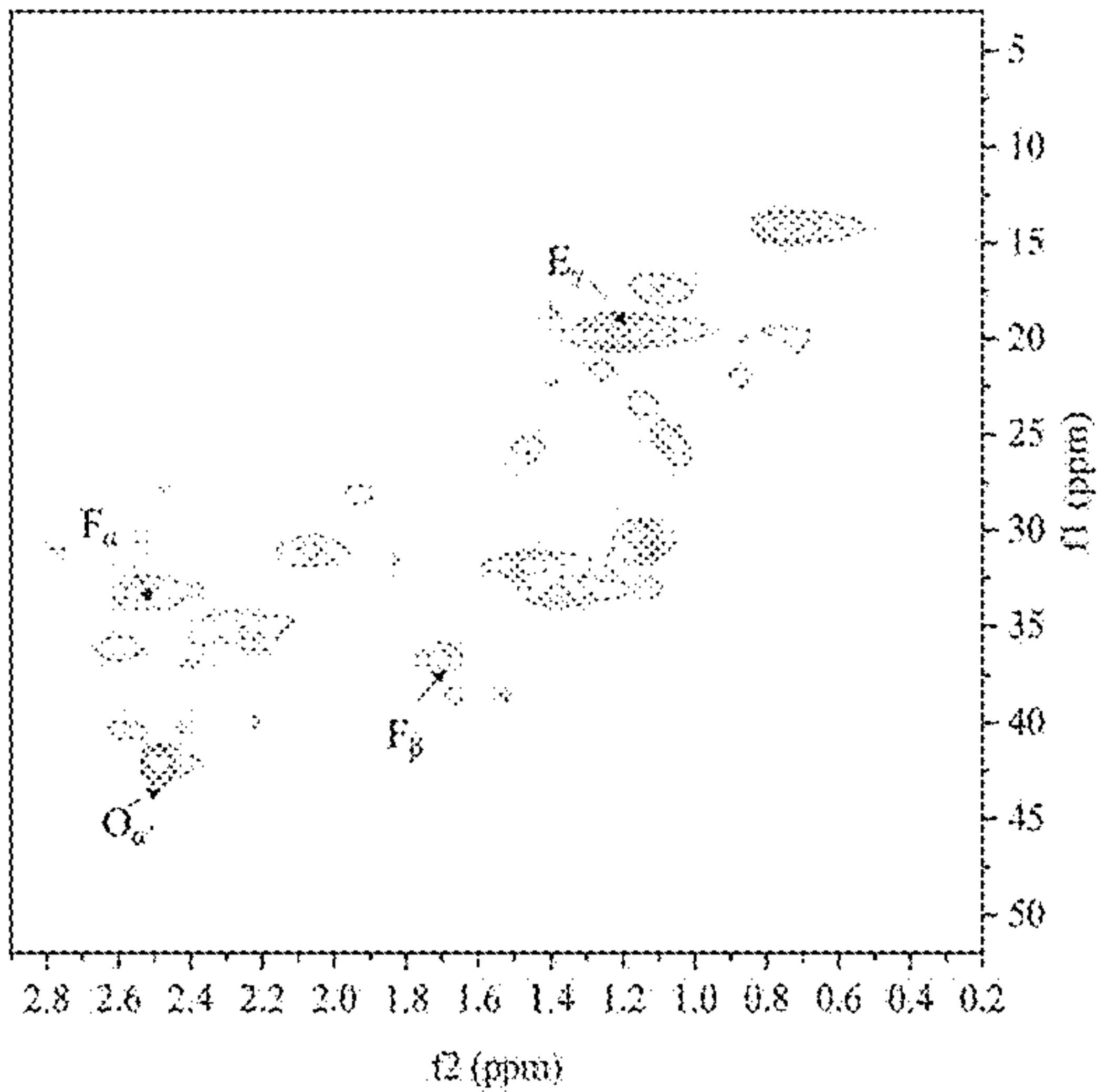


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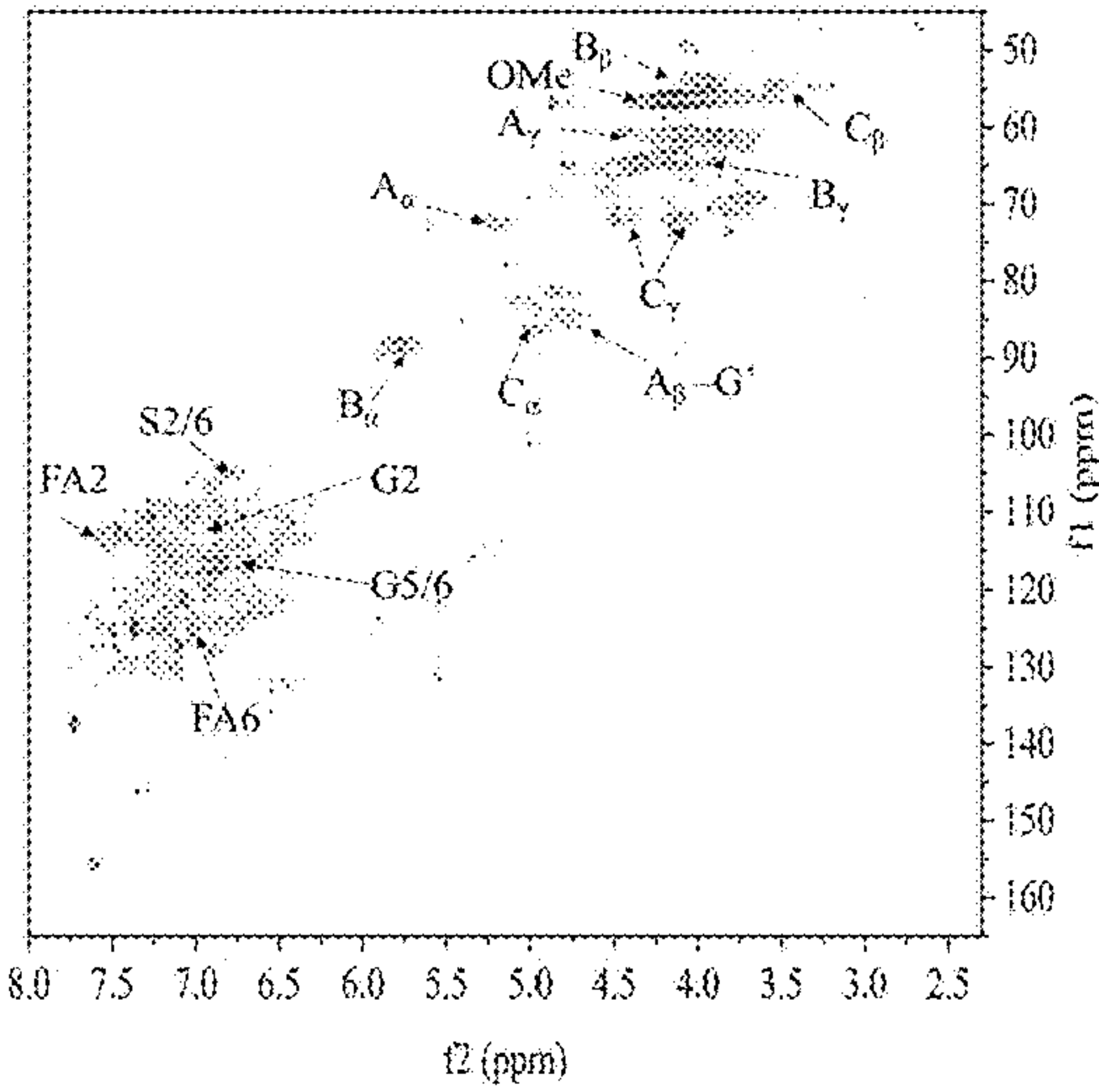


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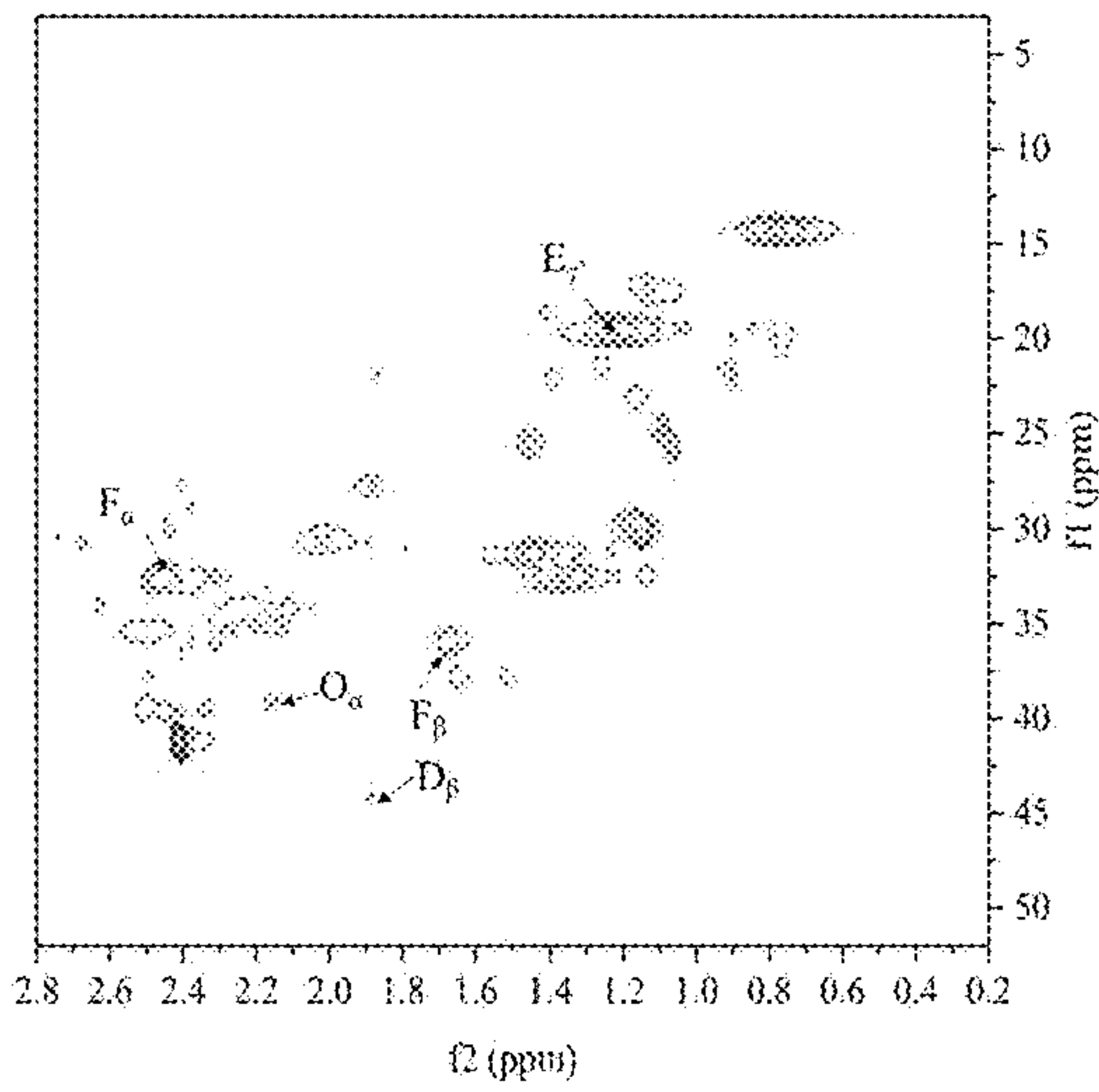


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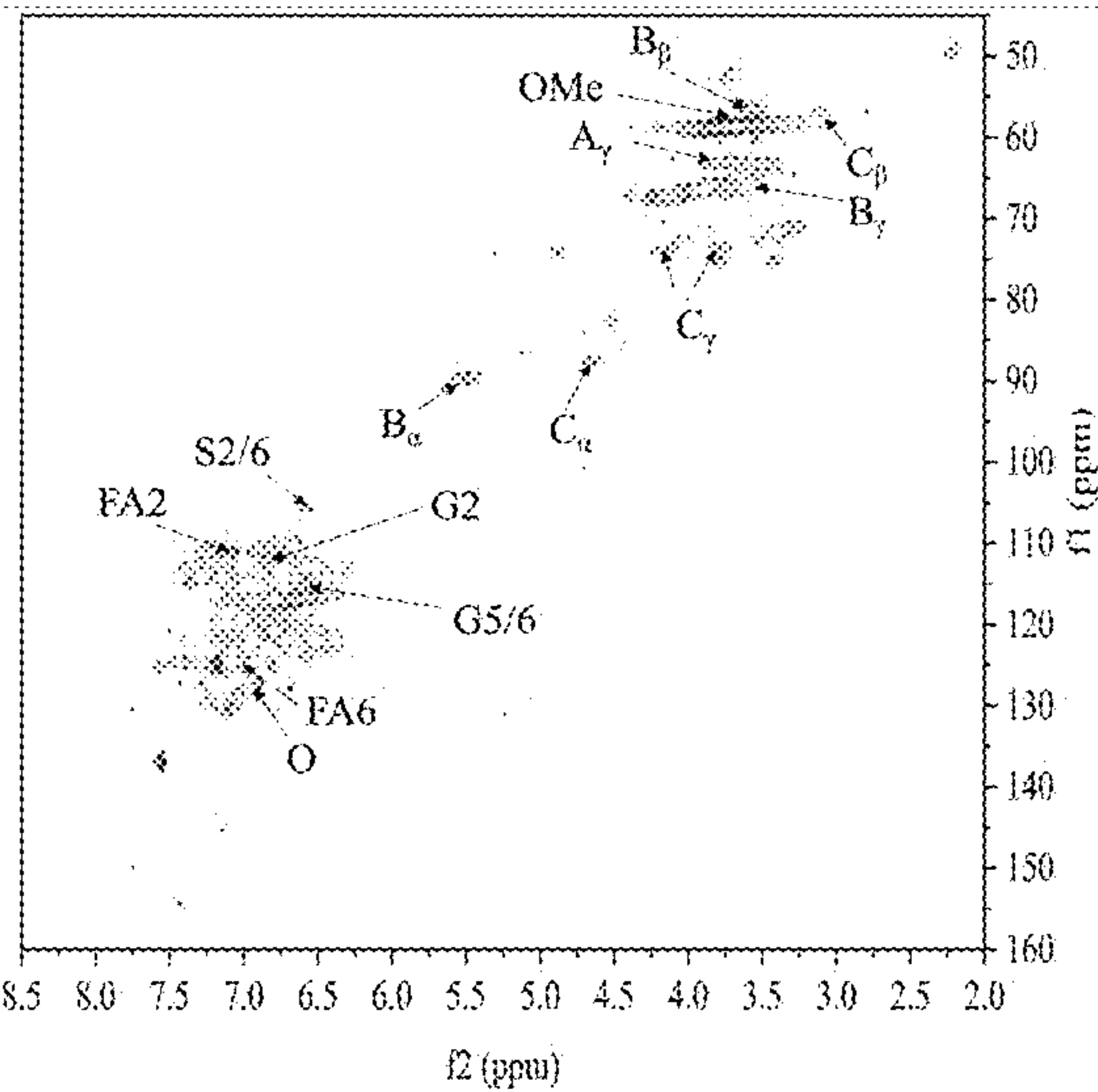


Figure 10G

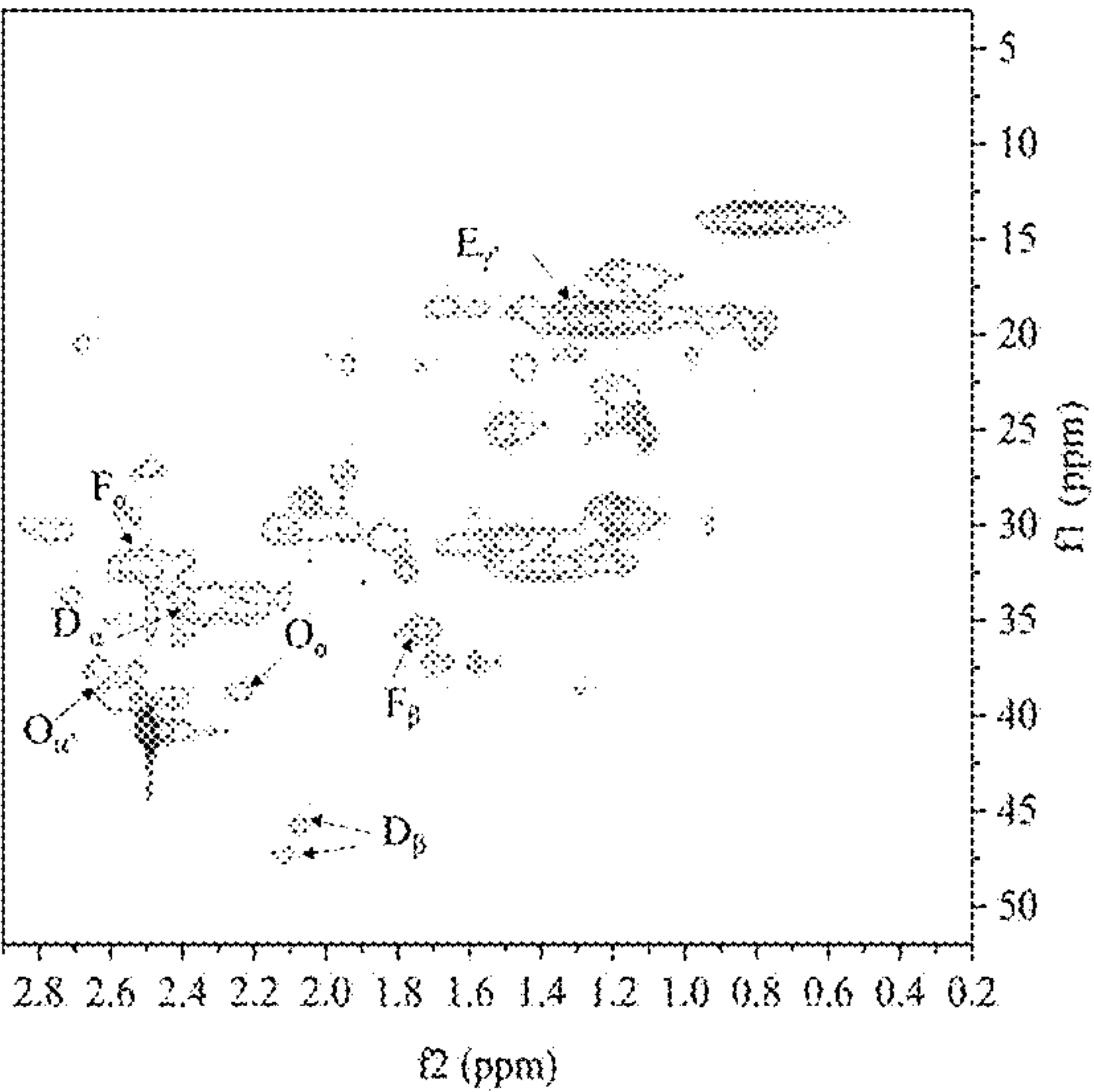


Figure 10H

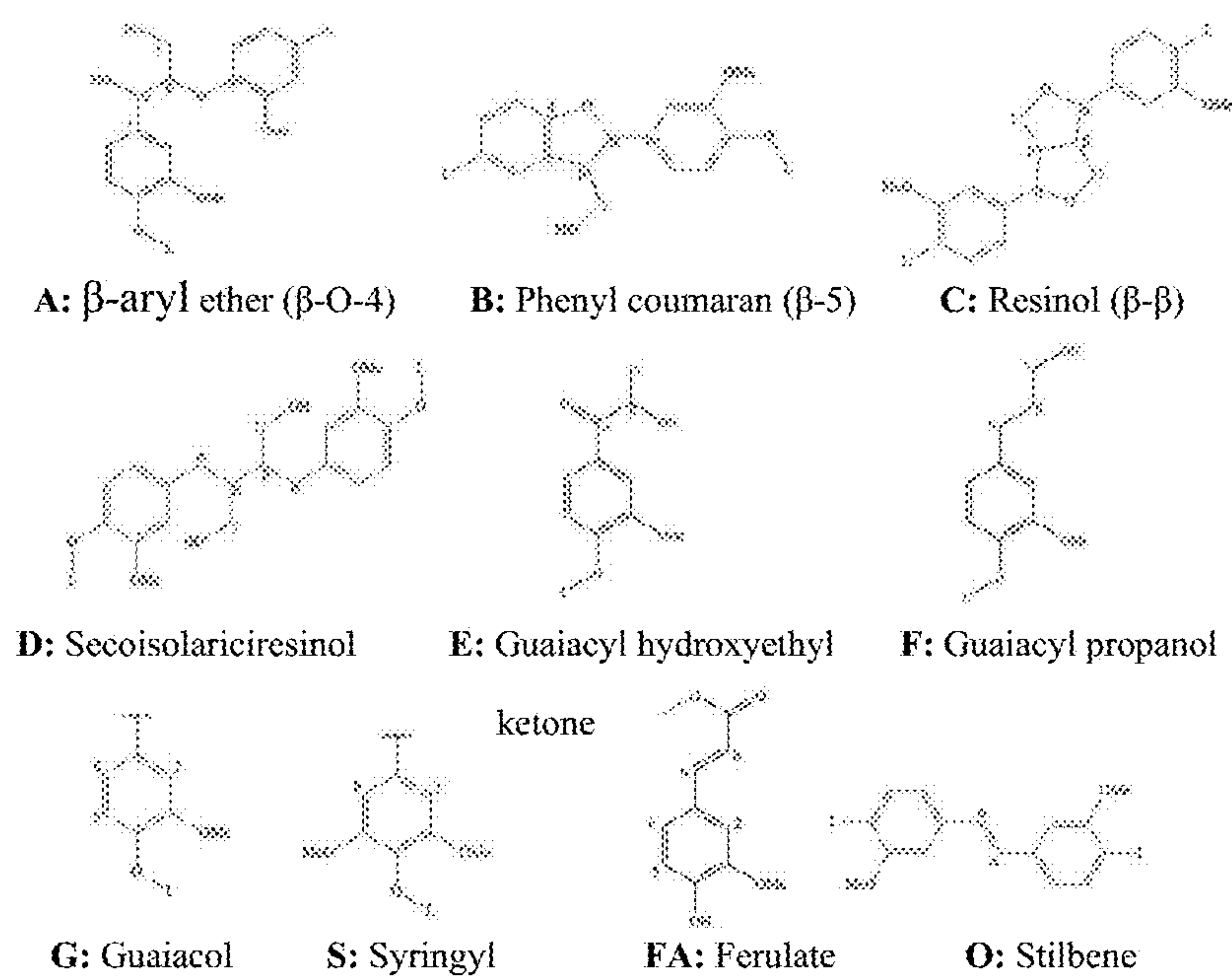


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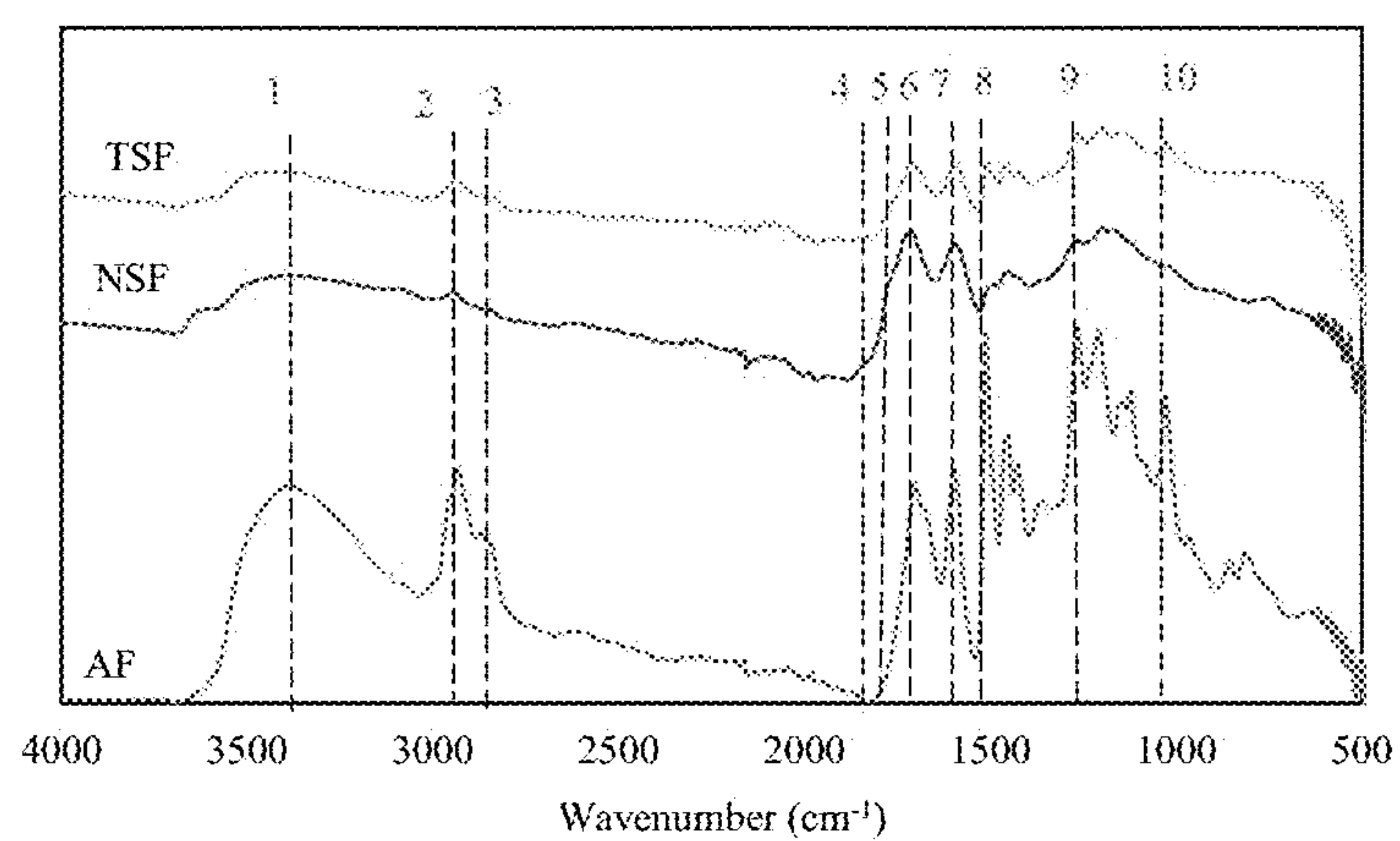


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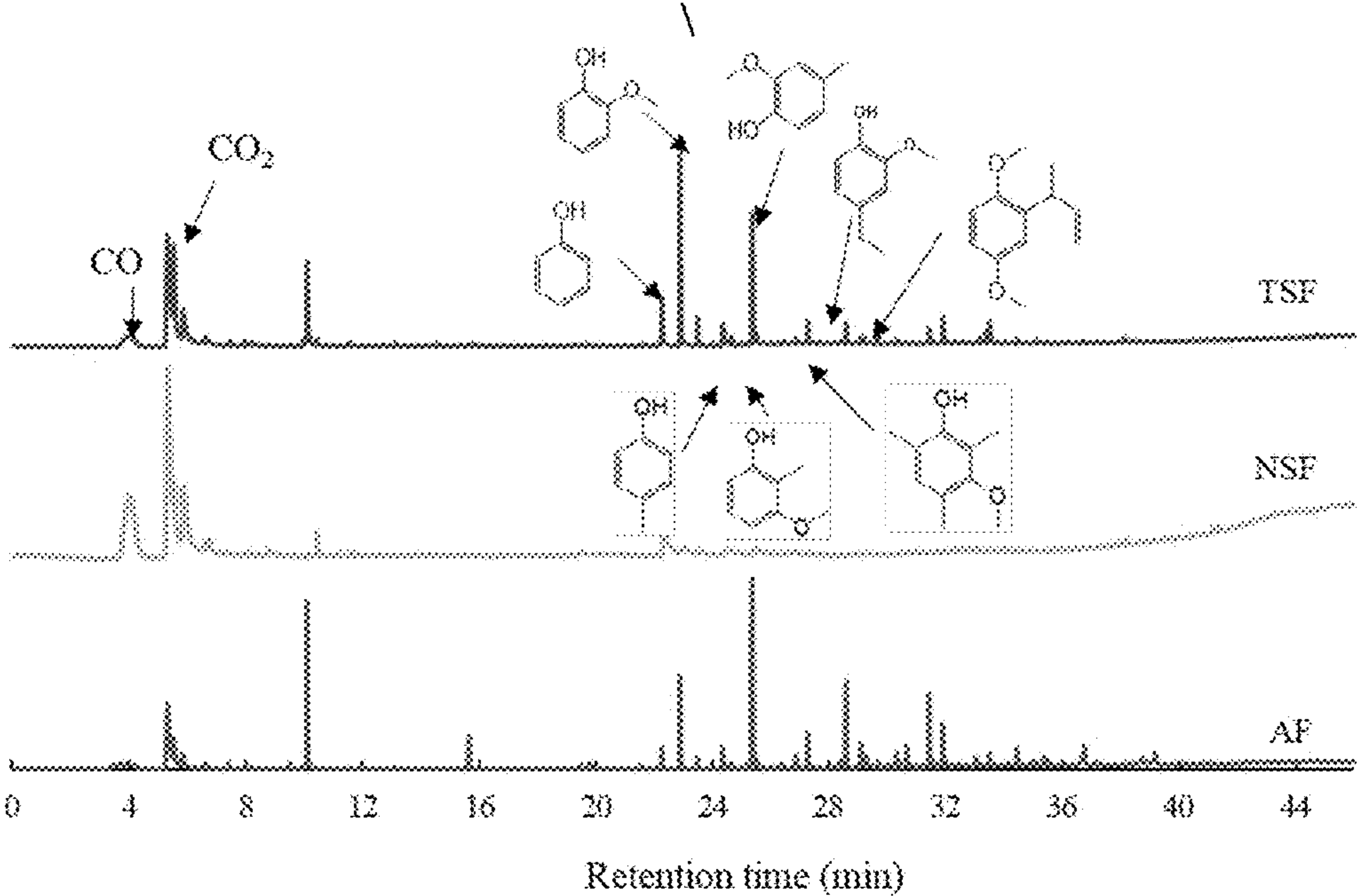


Figure 12

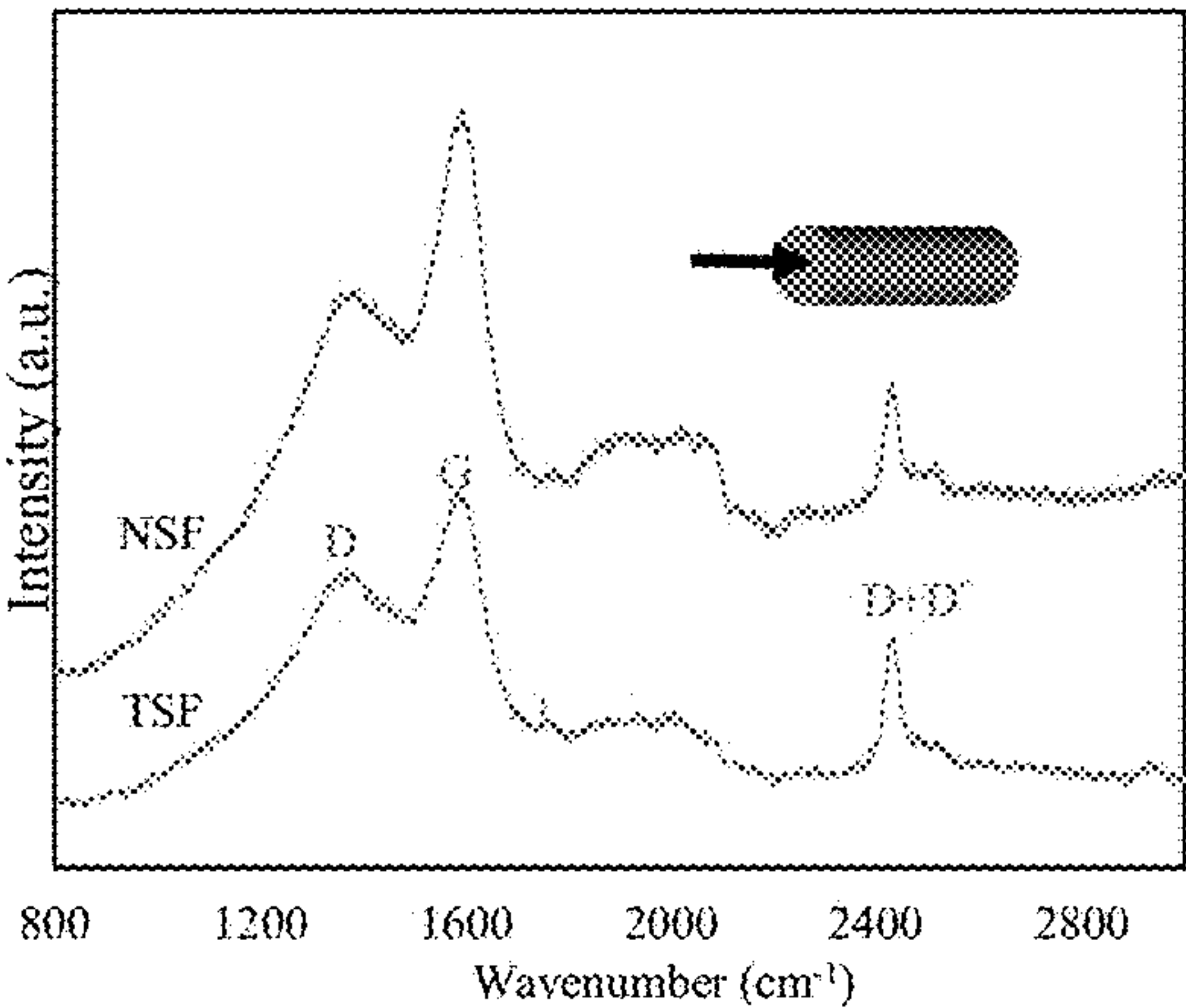


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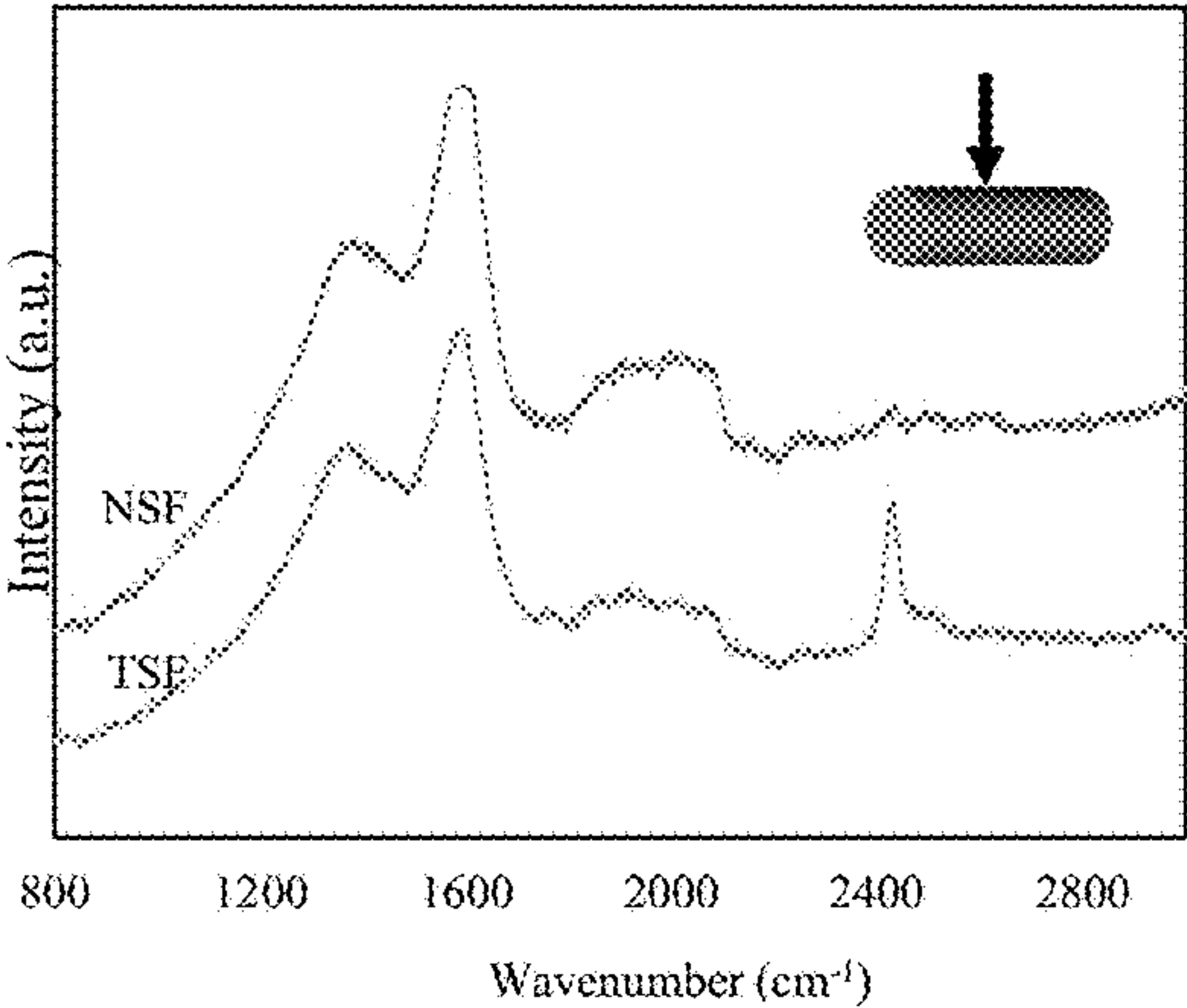


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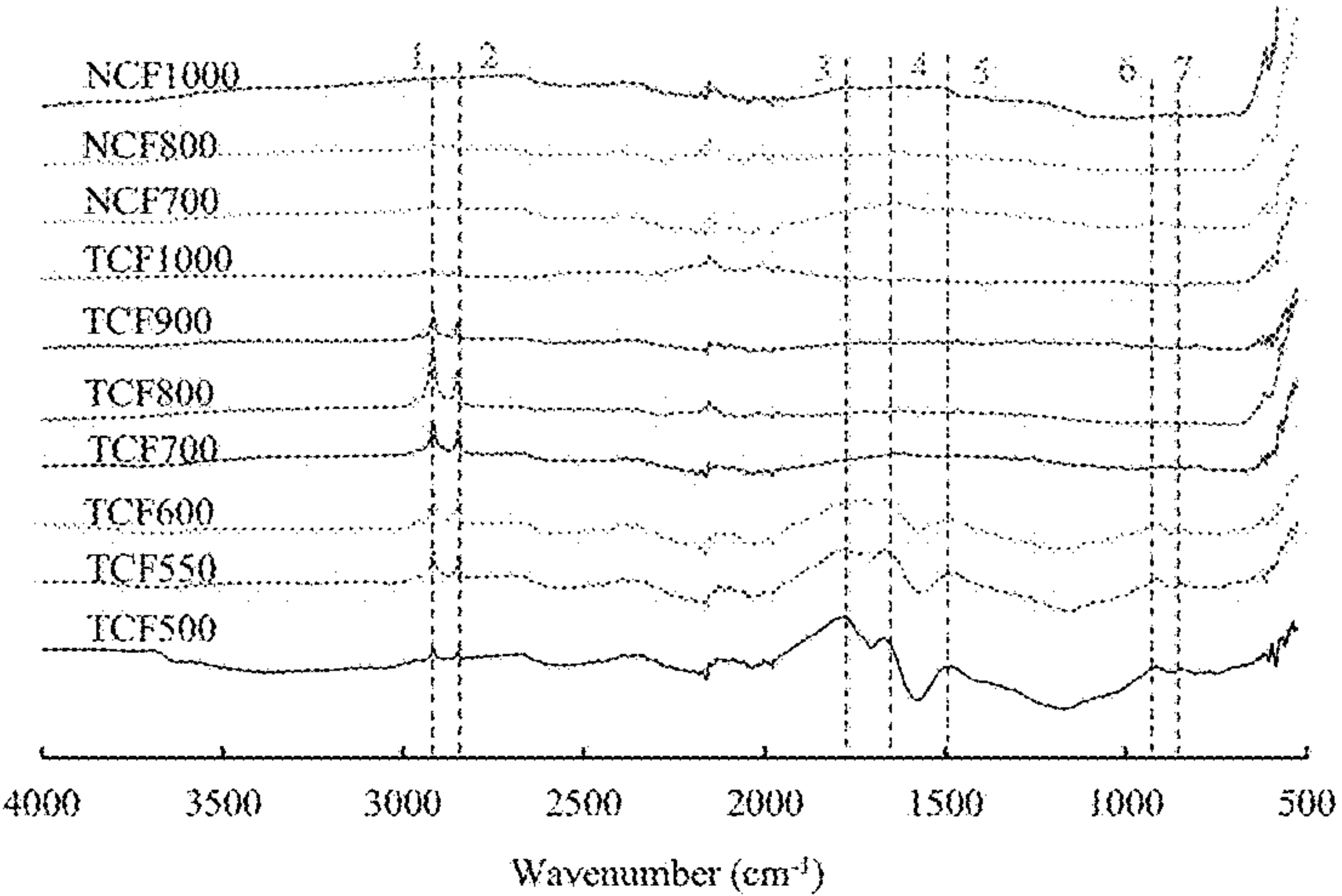


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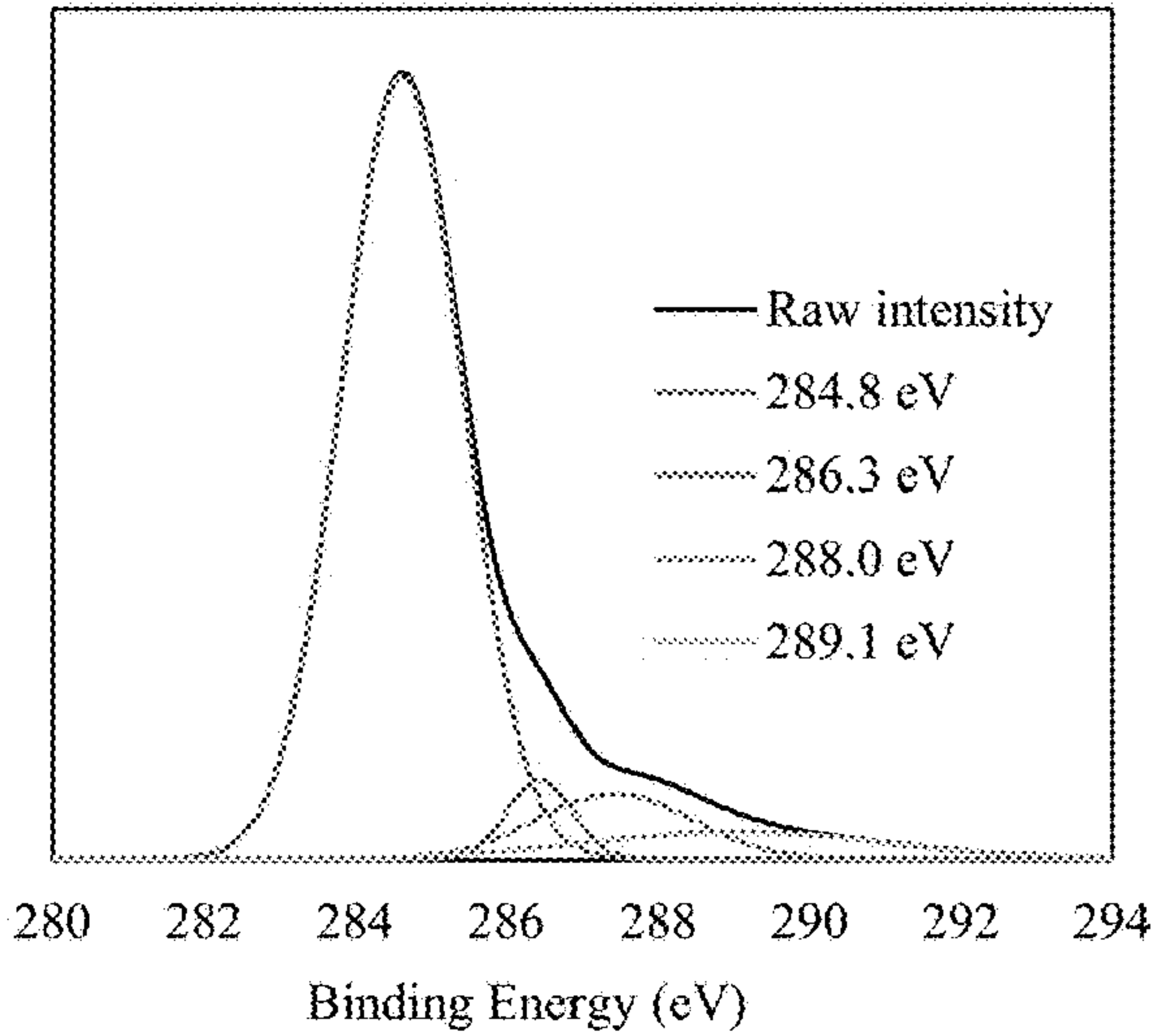


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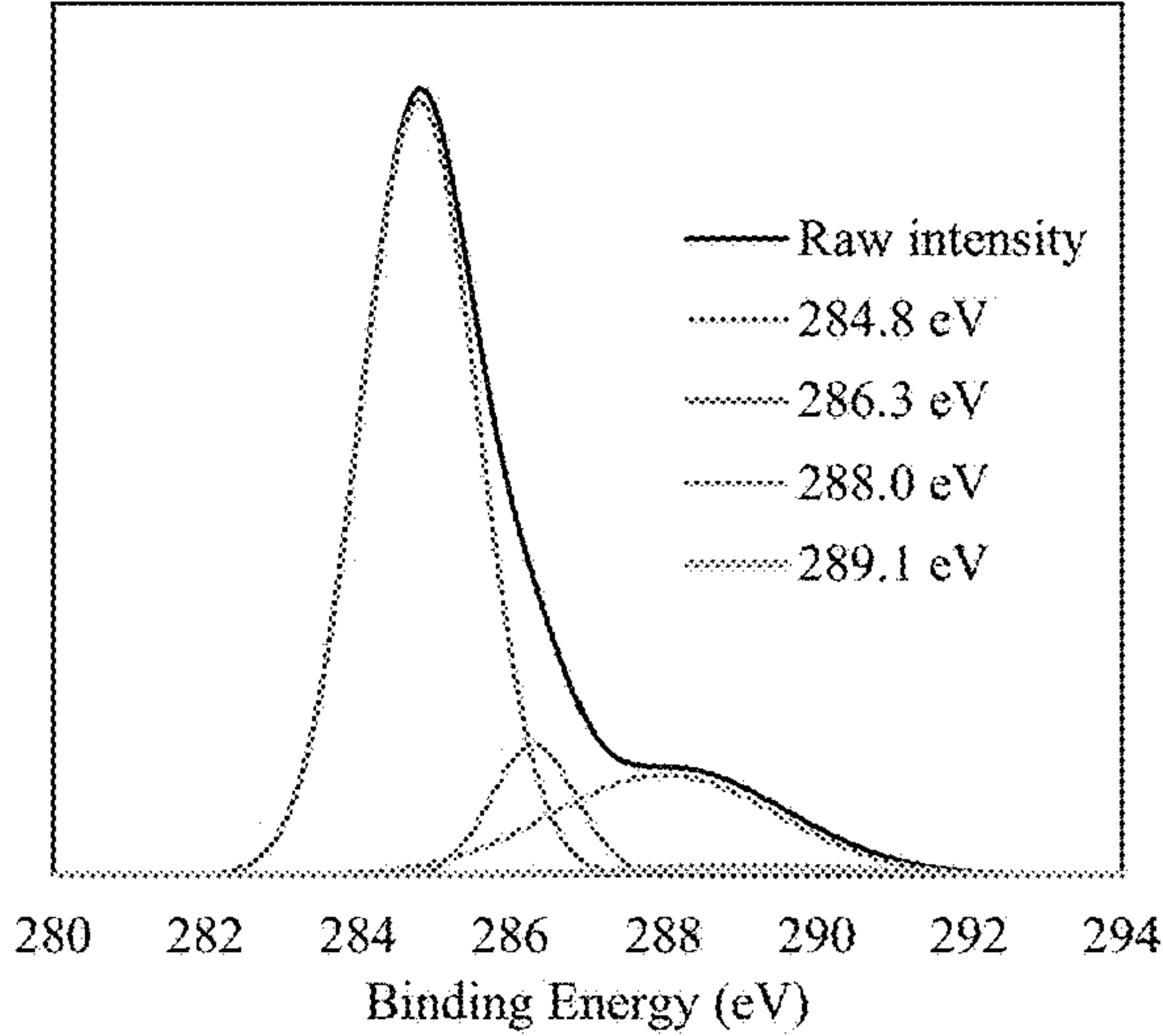


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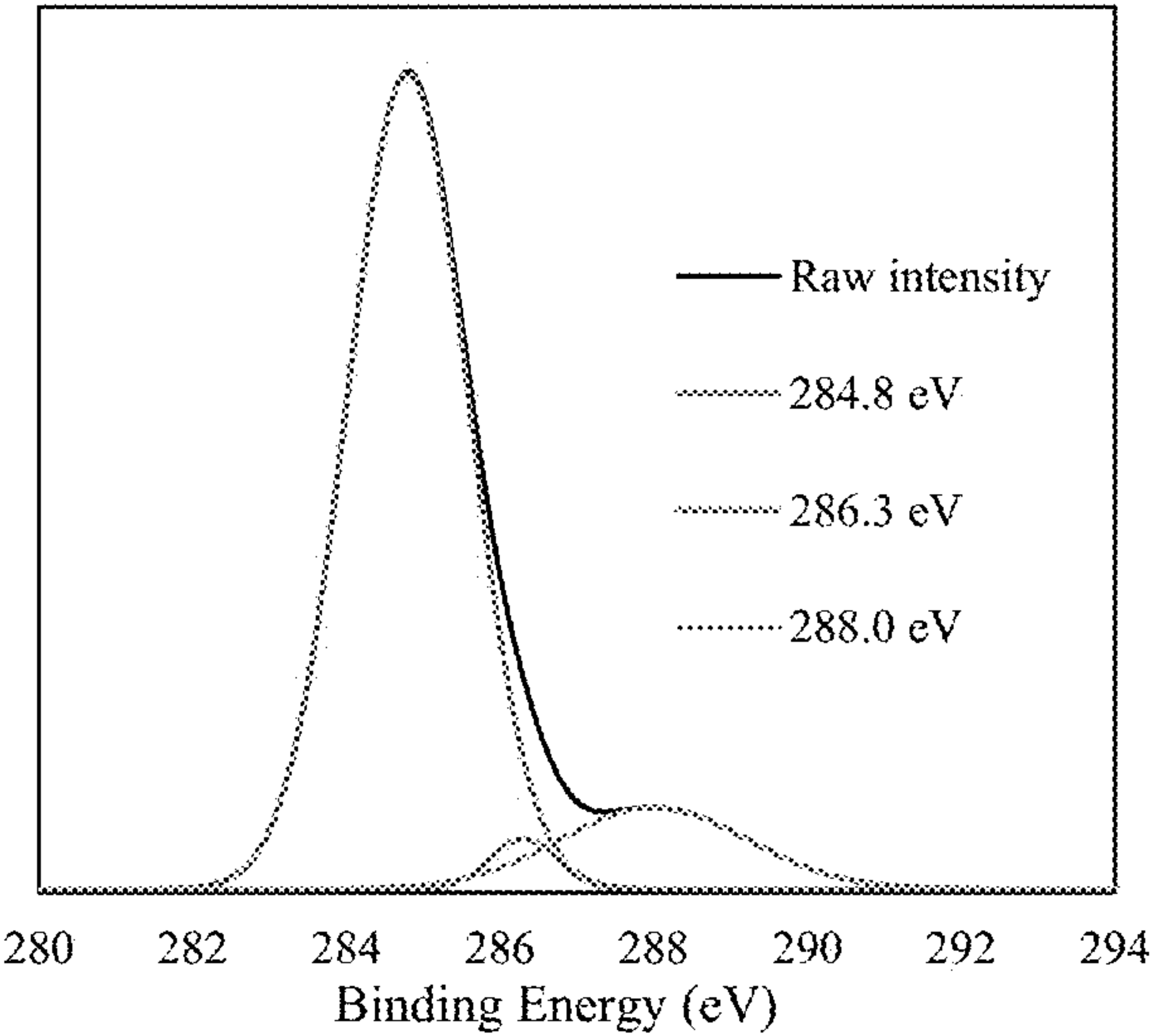


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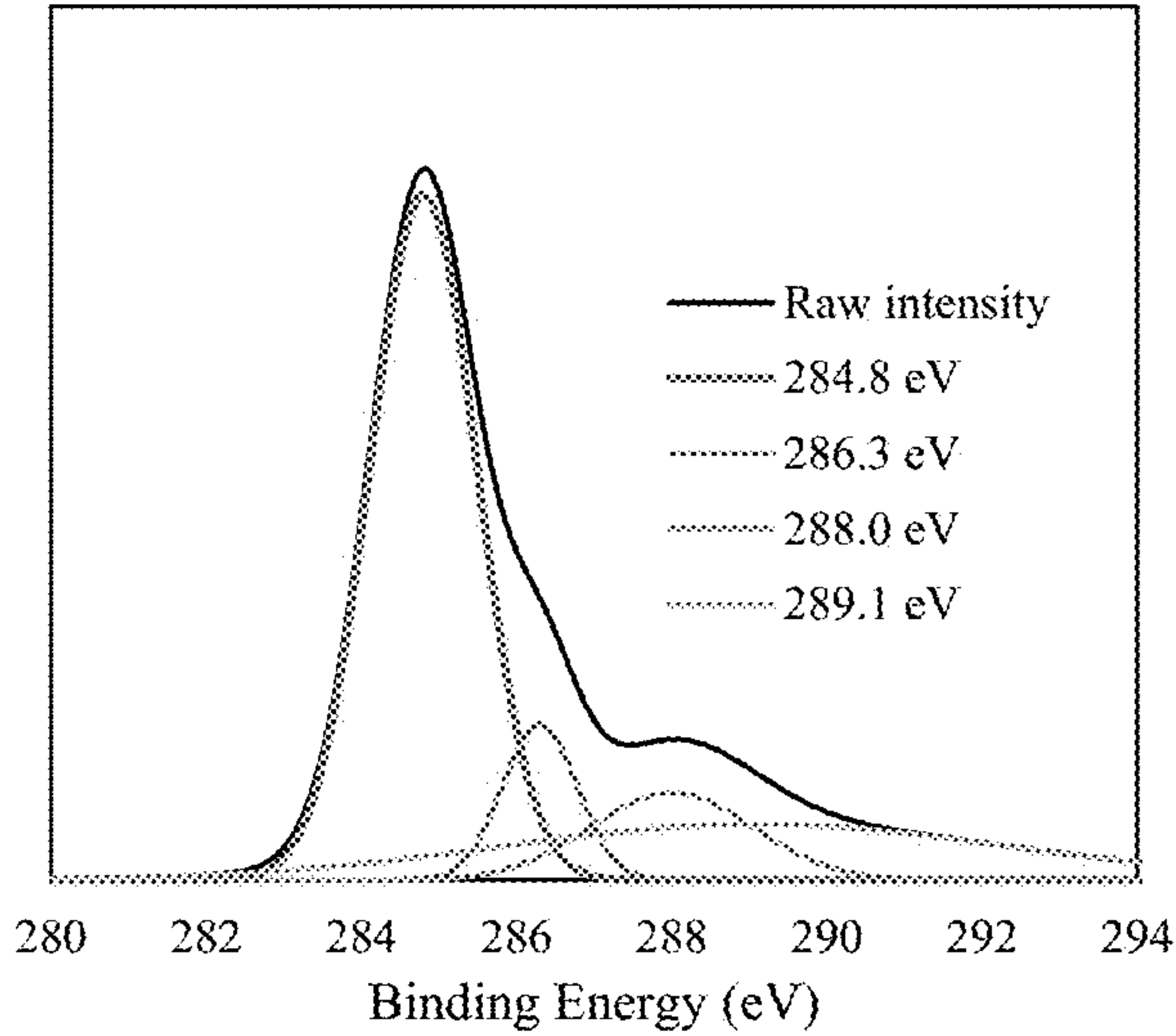


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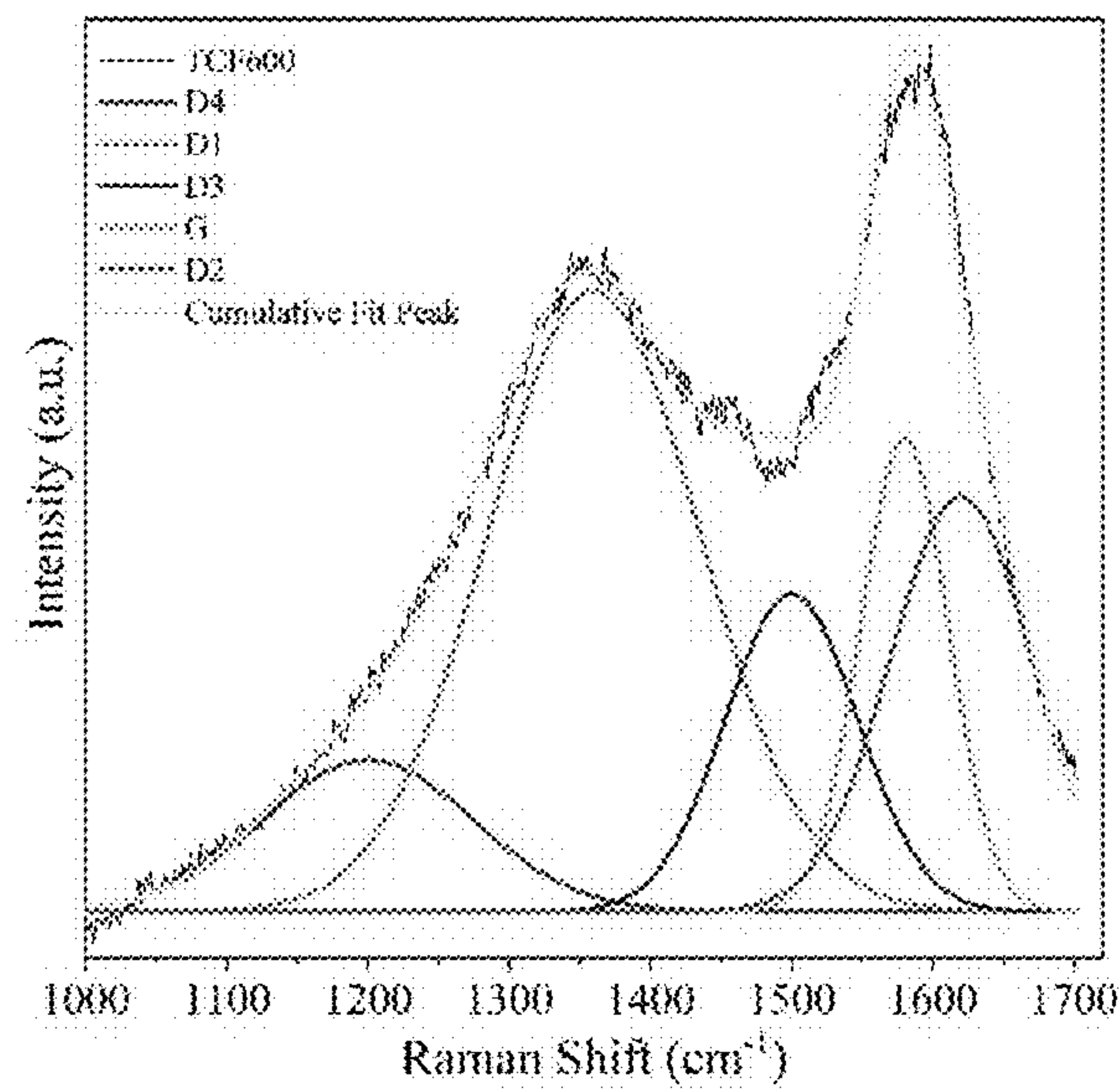


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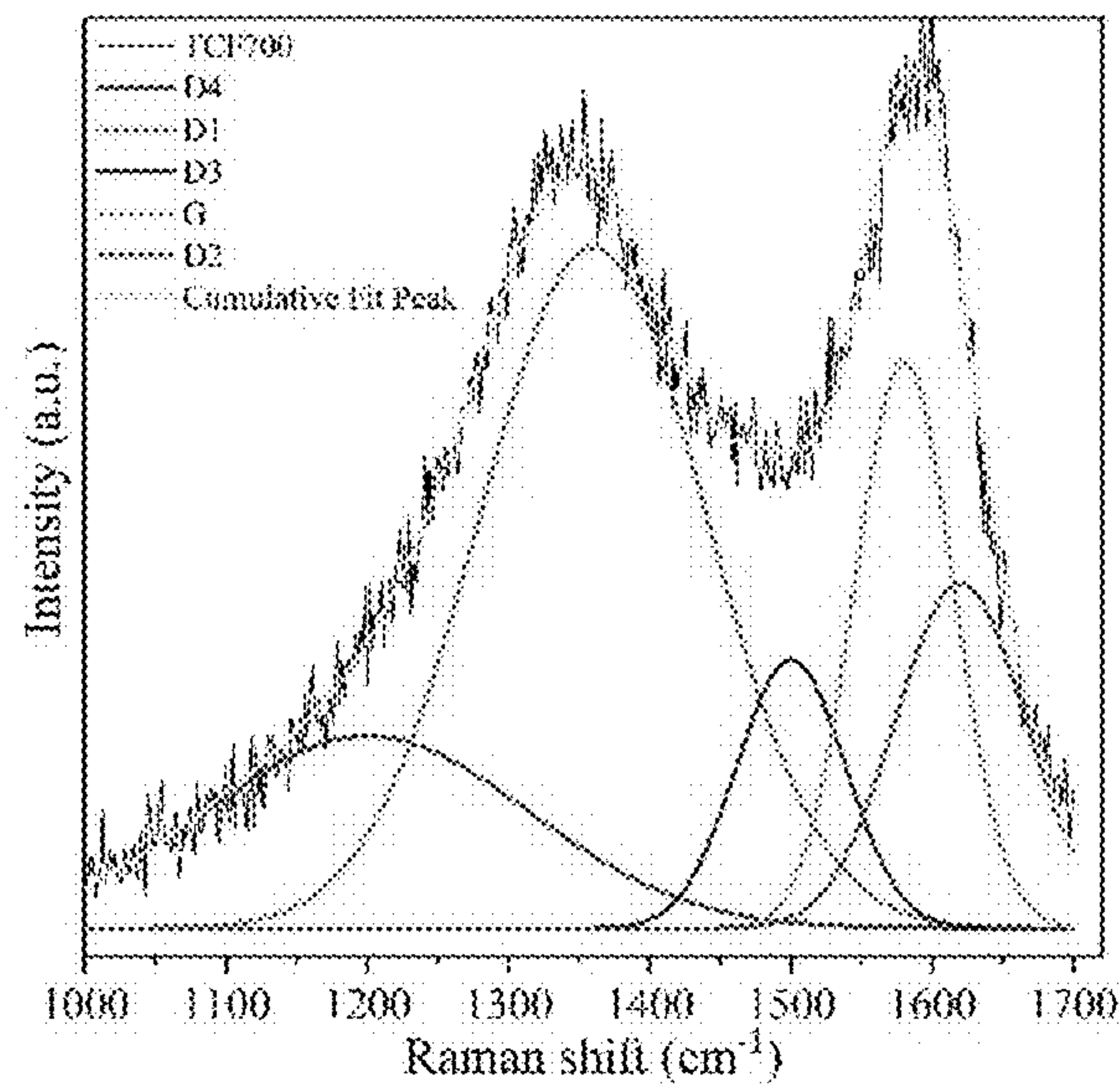


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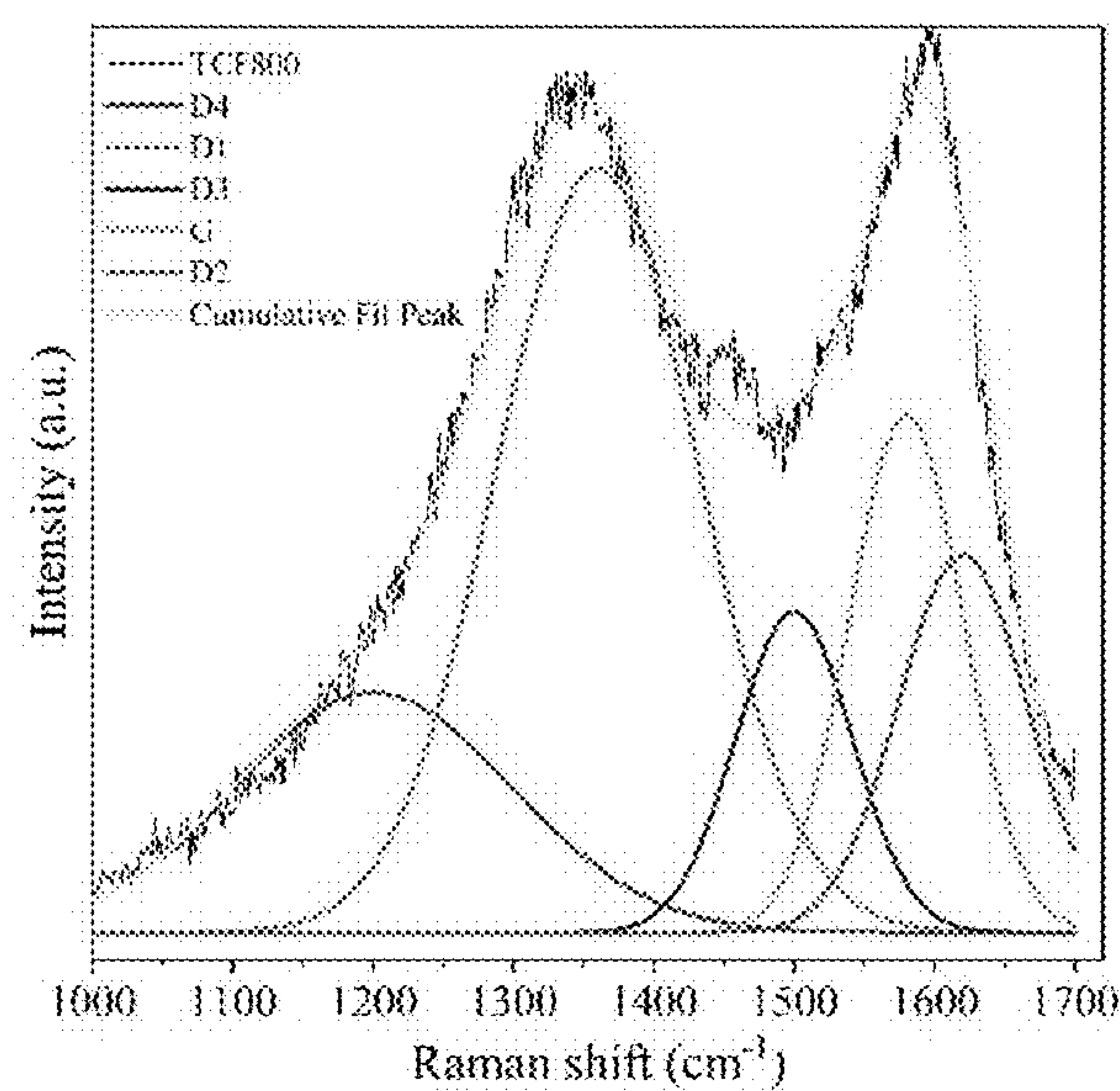


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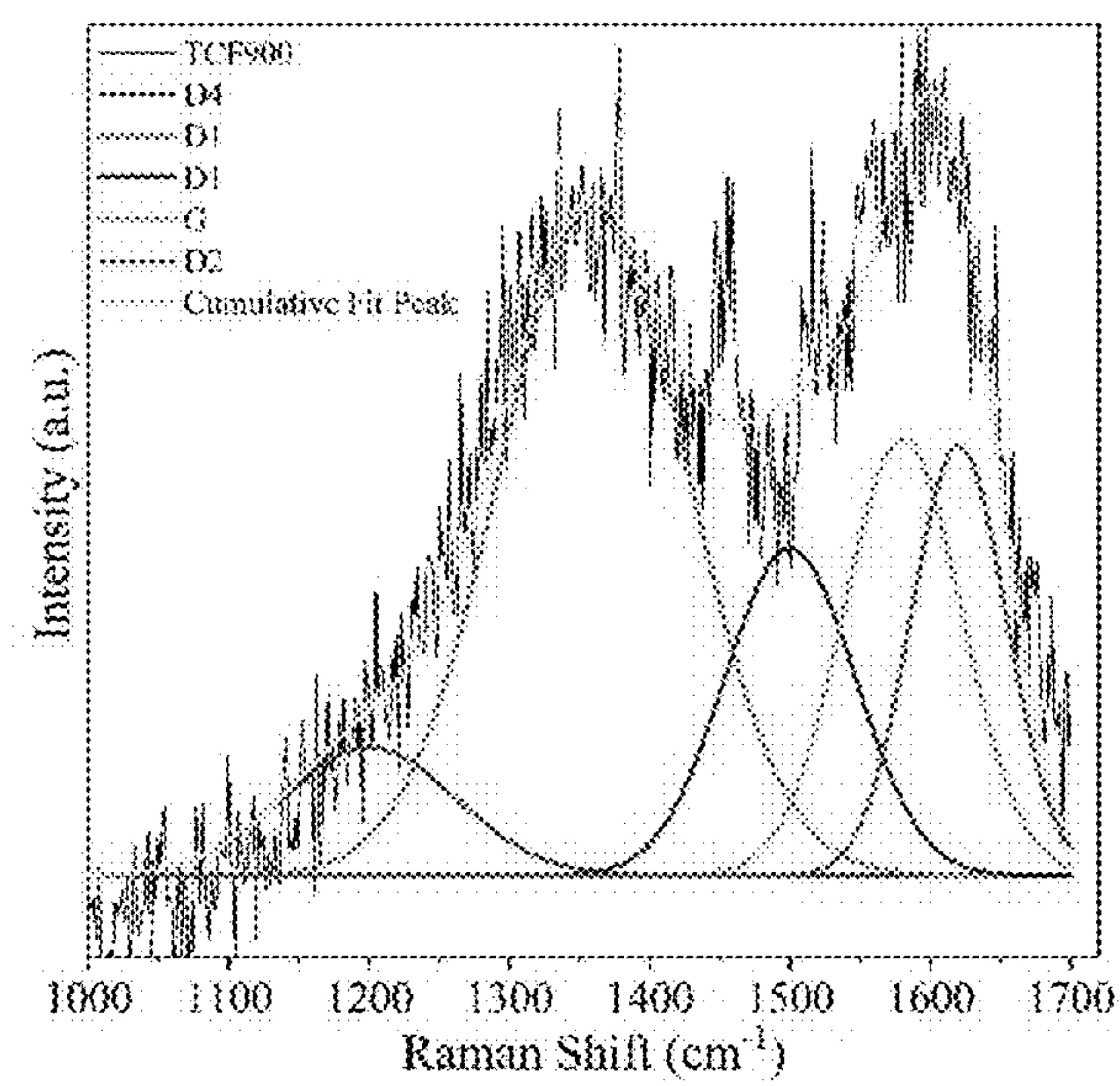


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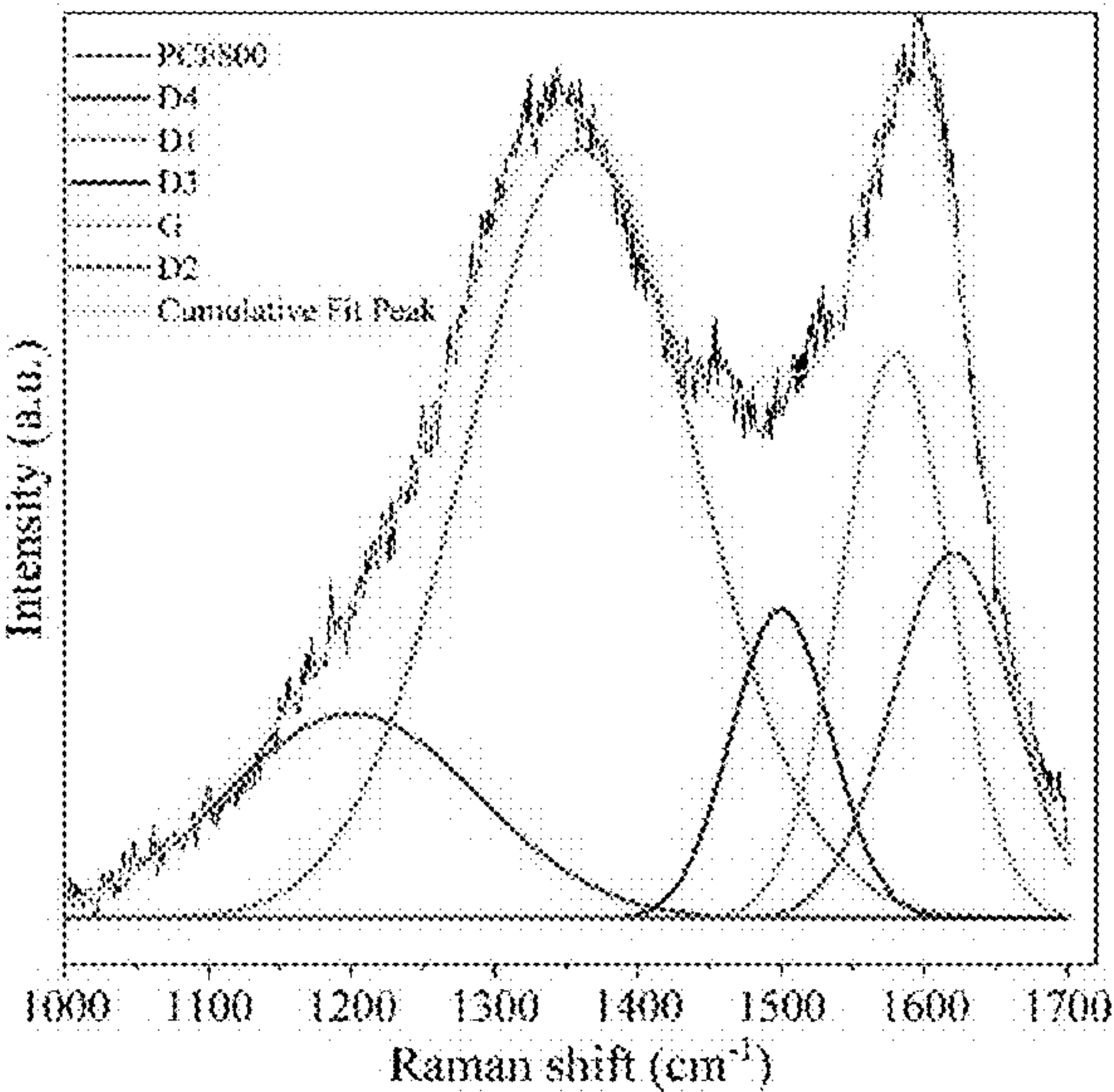


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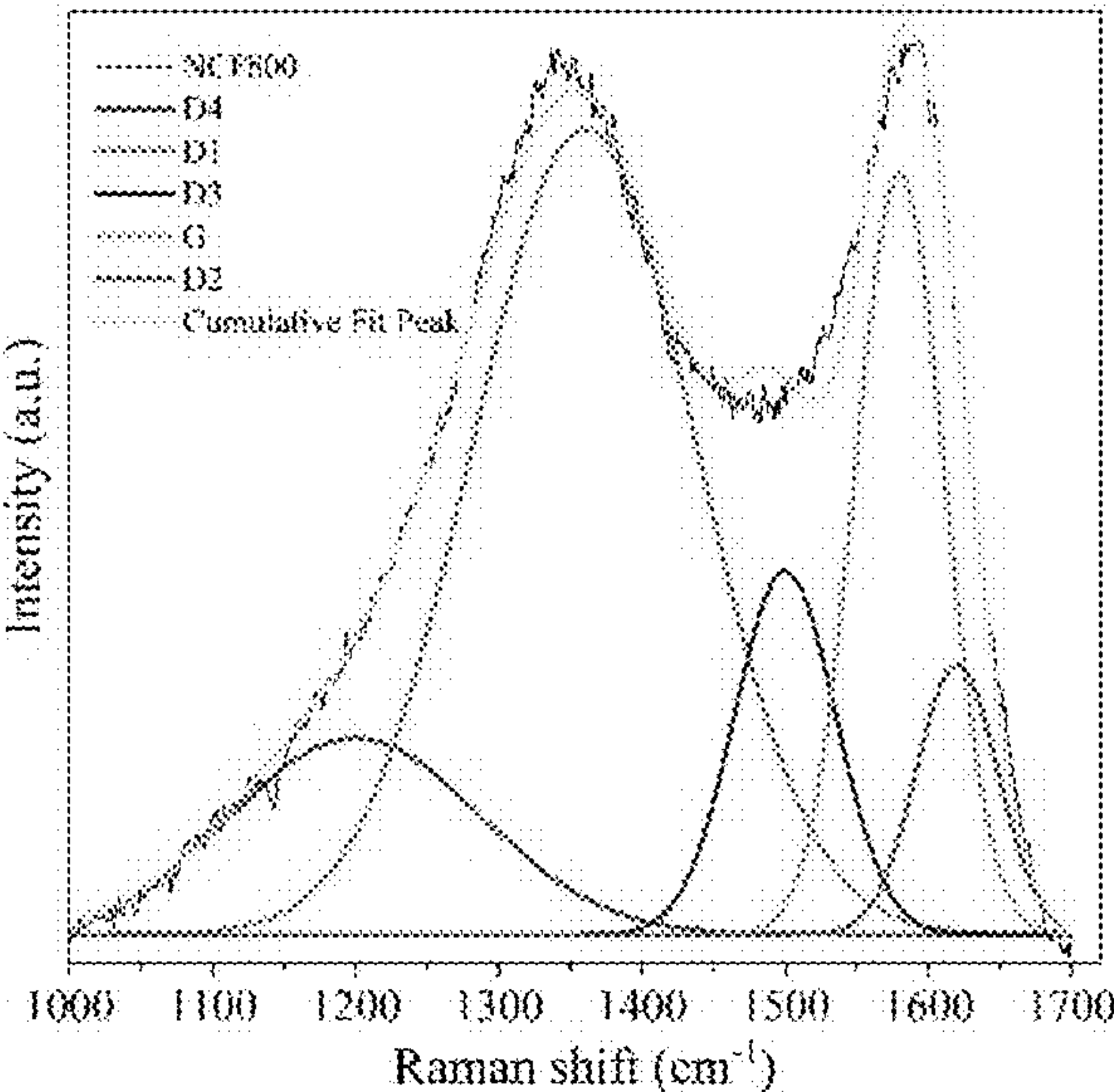


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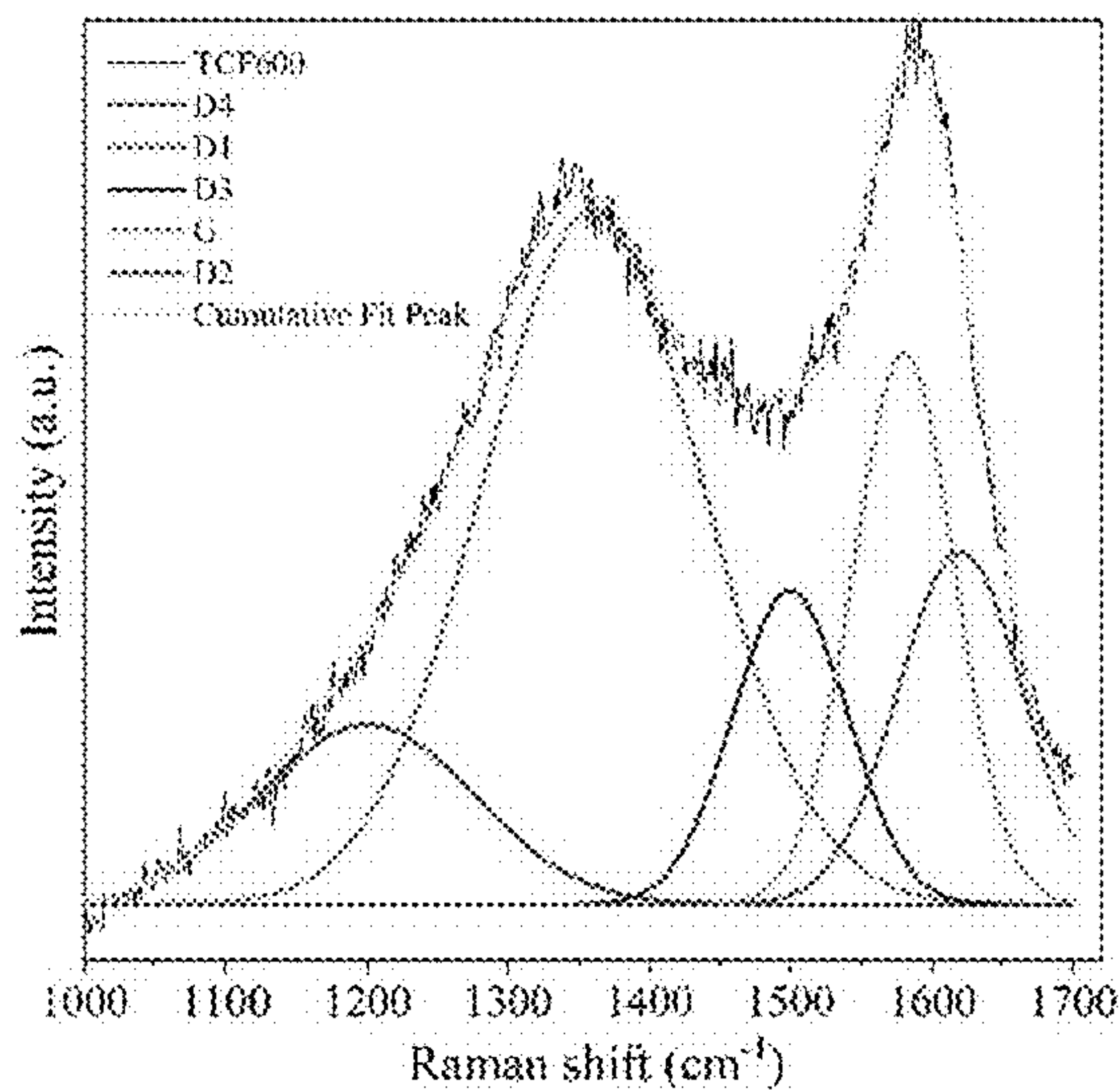


Figure 16G

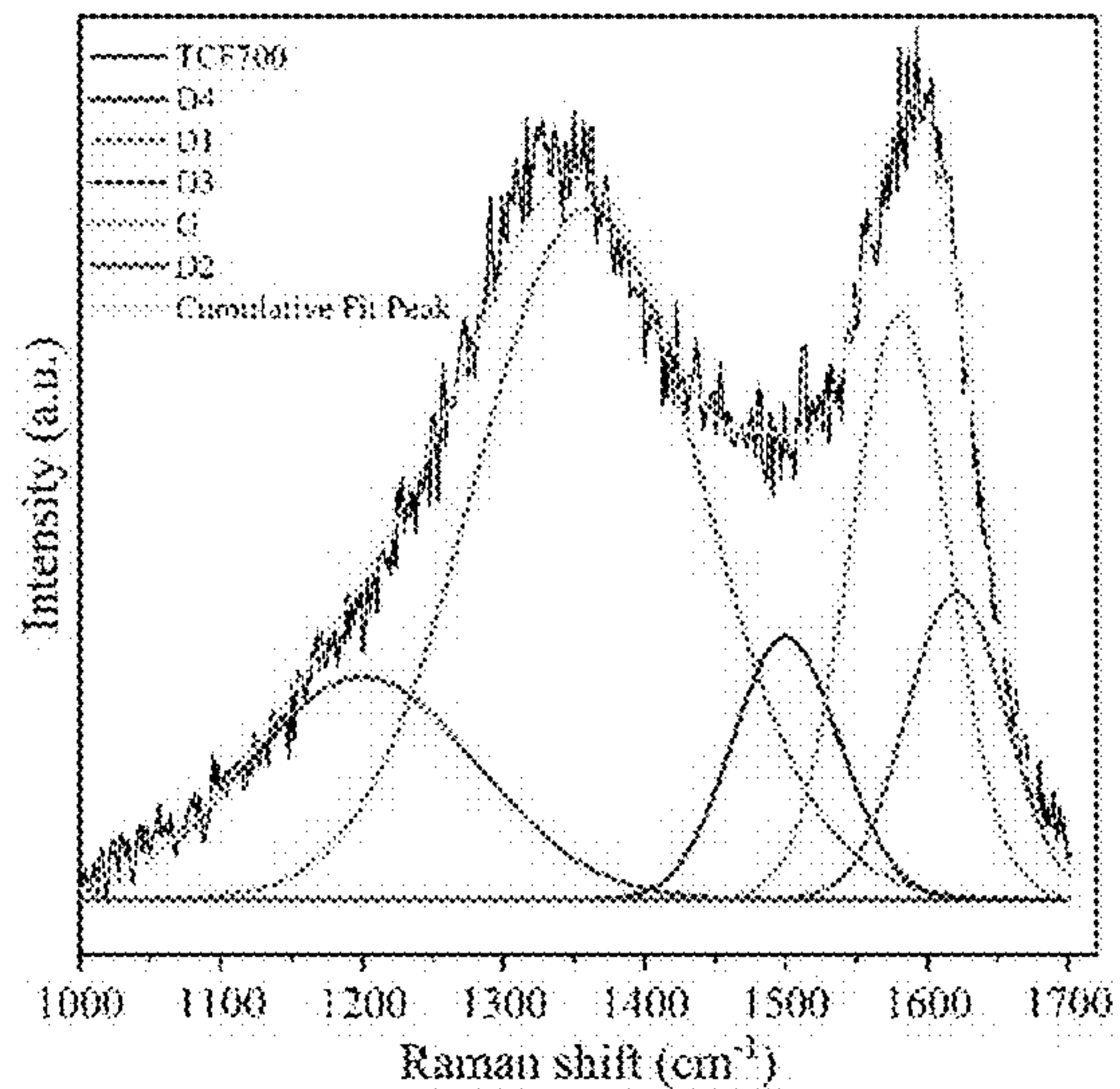


Figure 16H

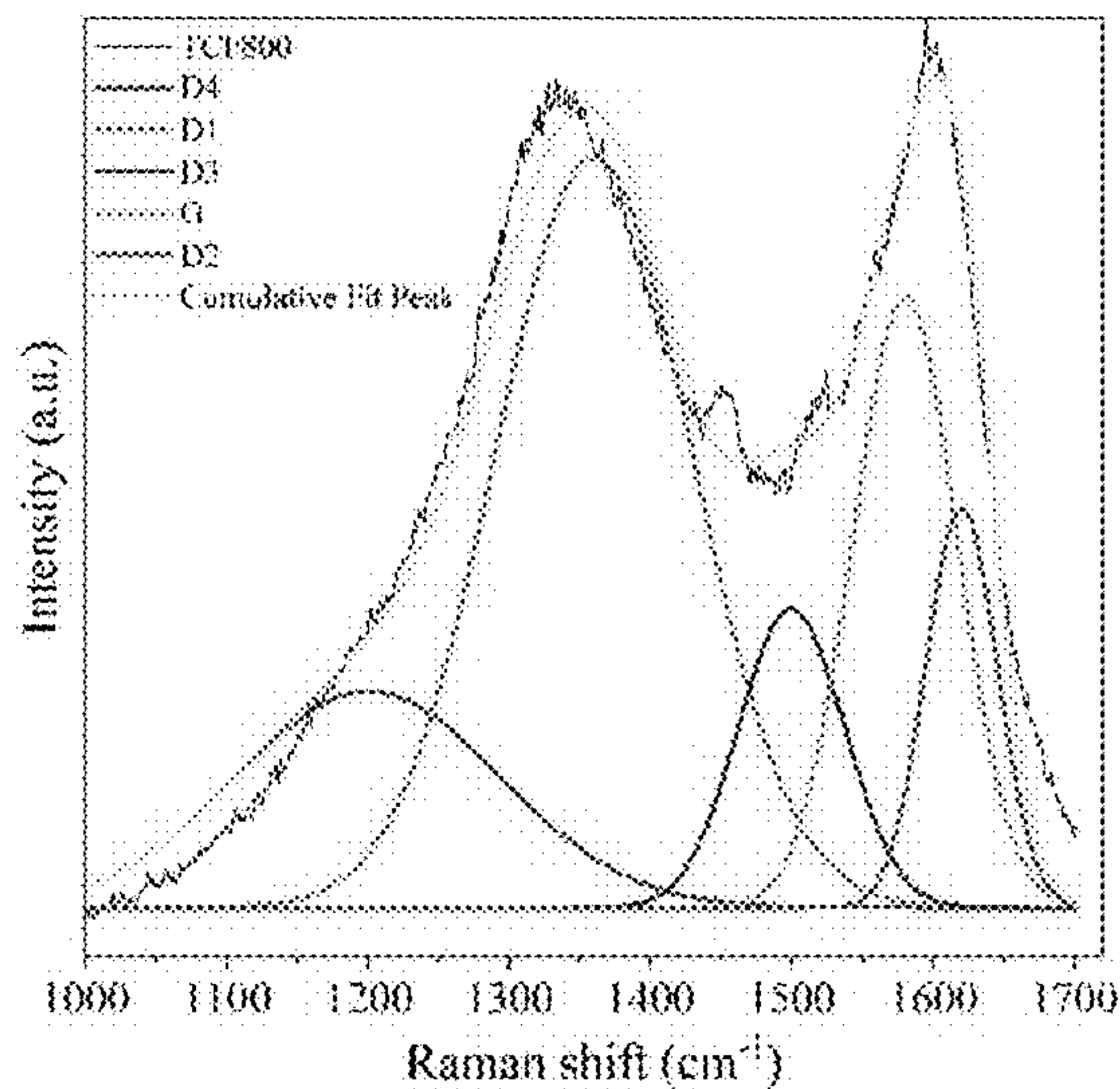


Figure 16I

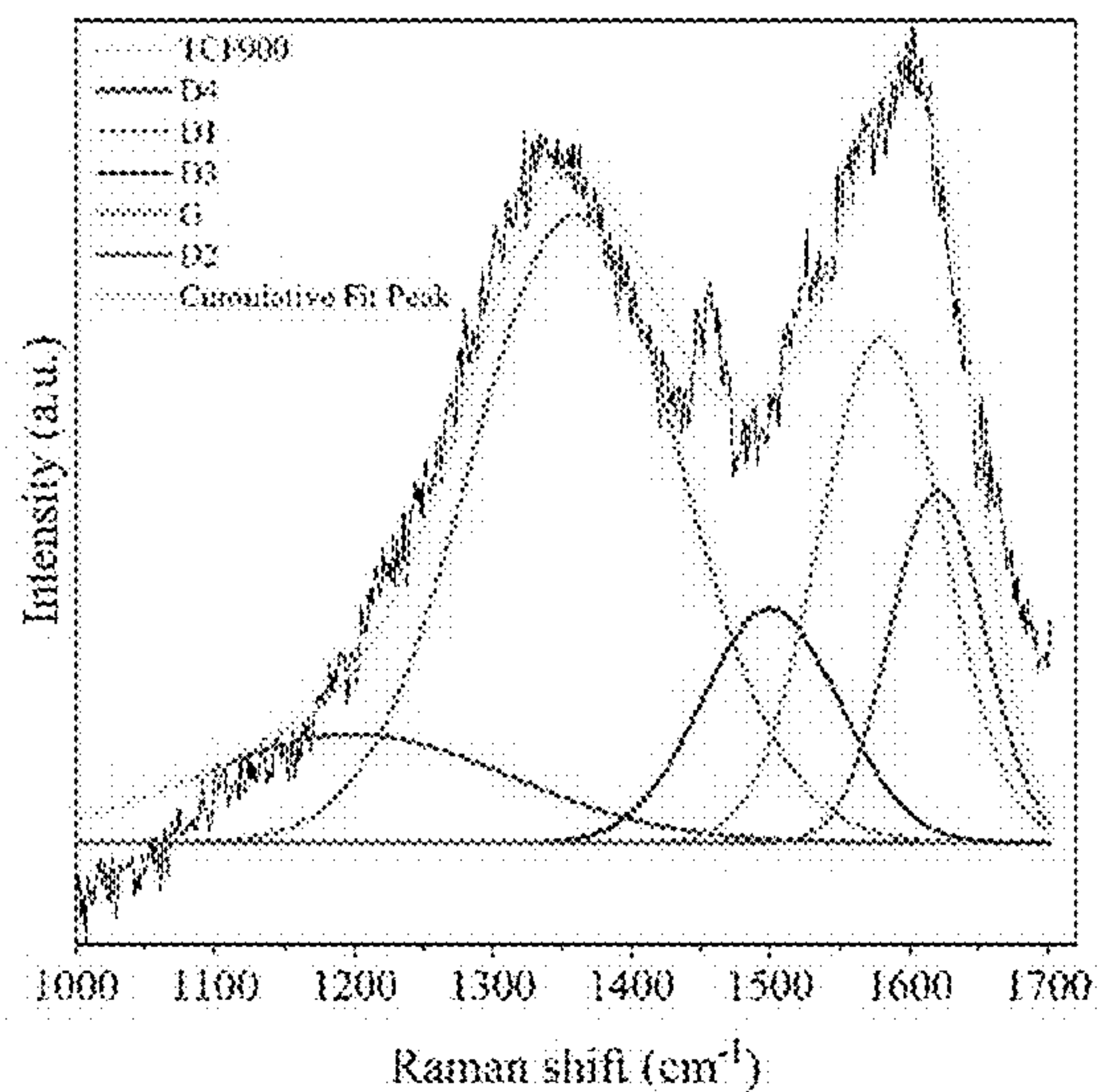


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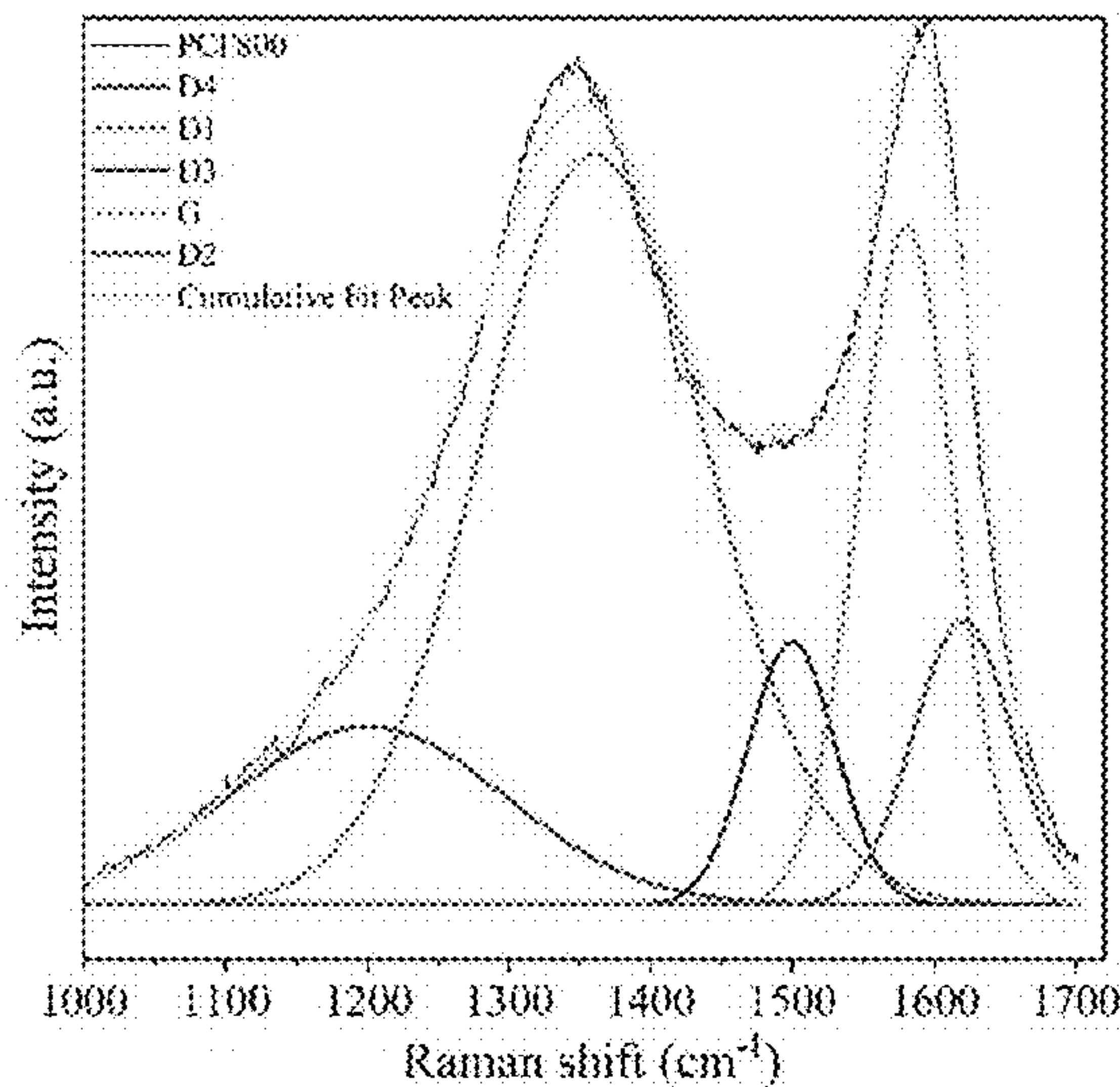
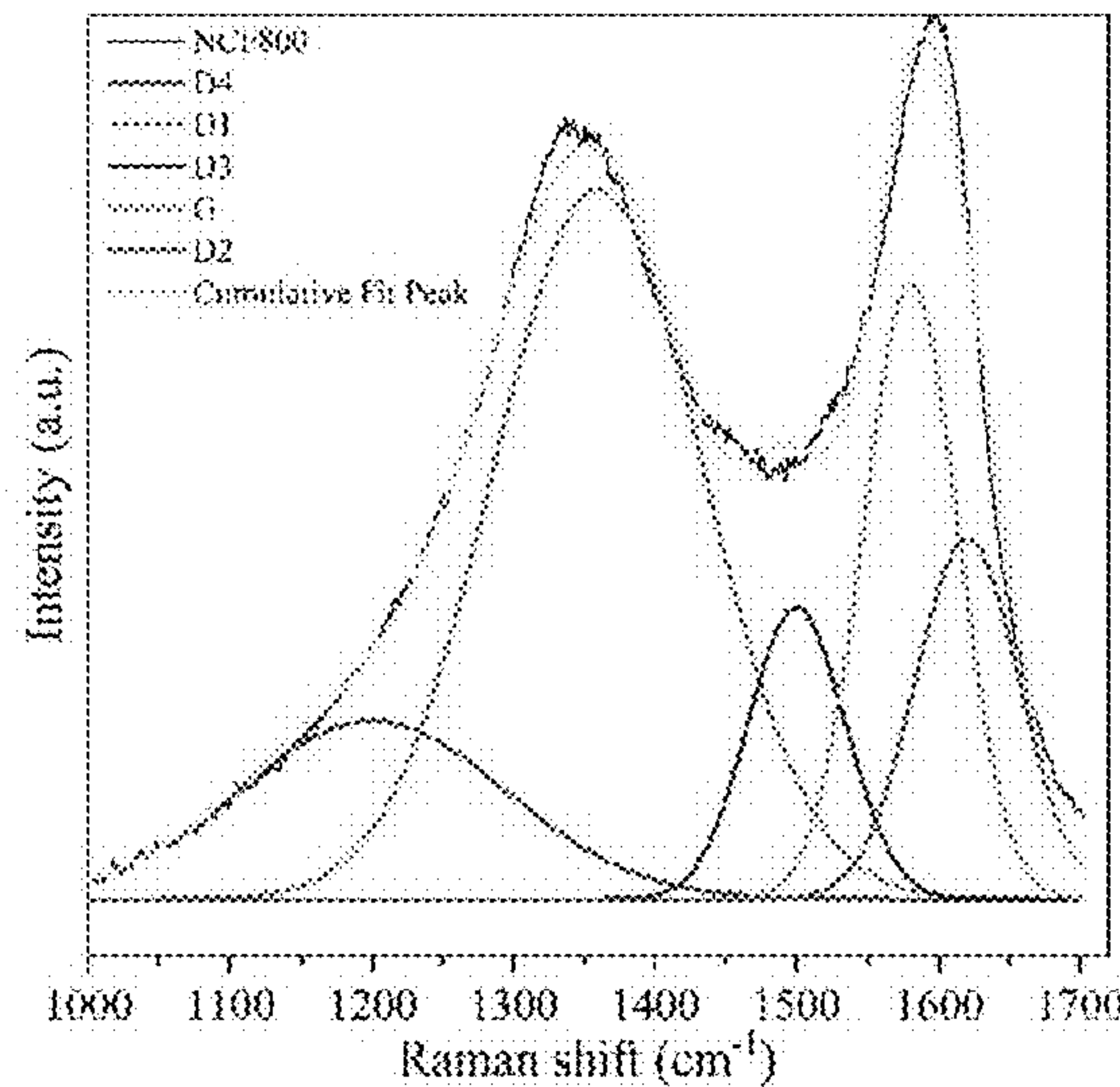


Figure 16K



Figures 16L

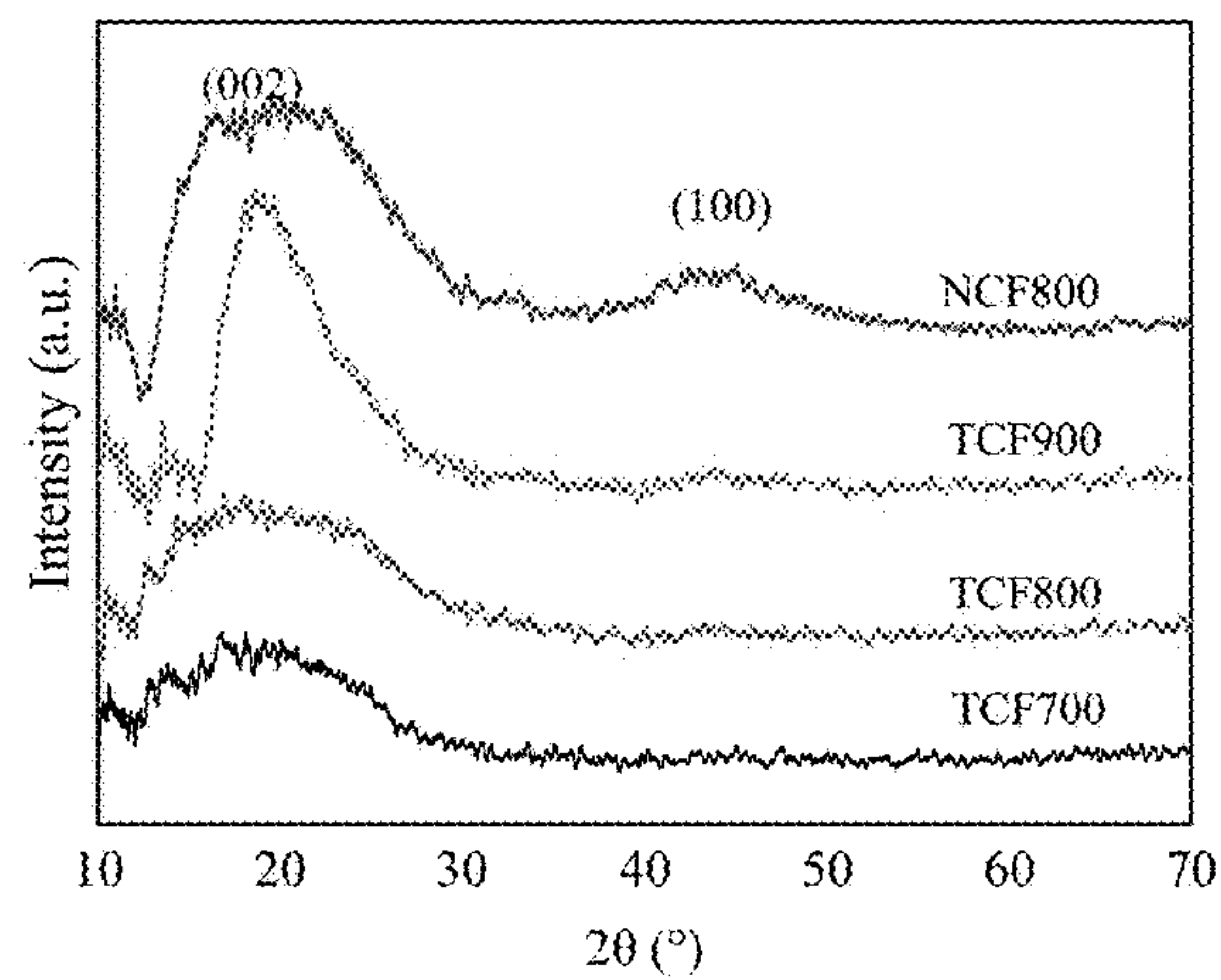


Figure 17A

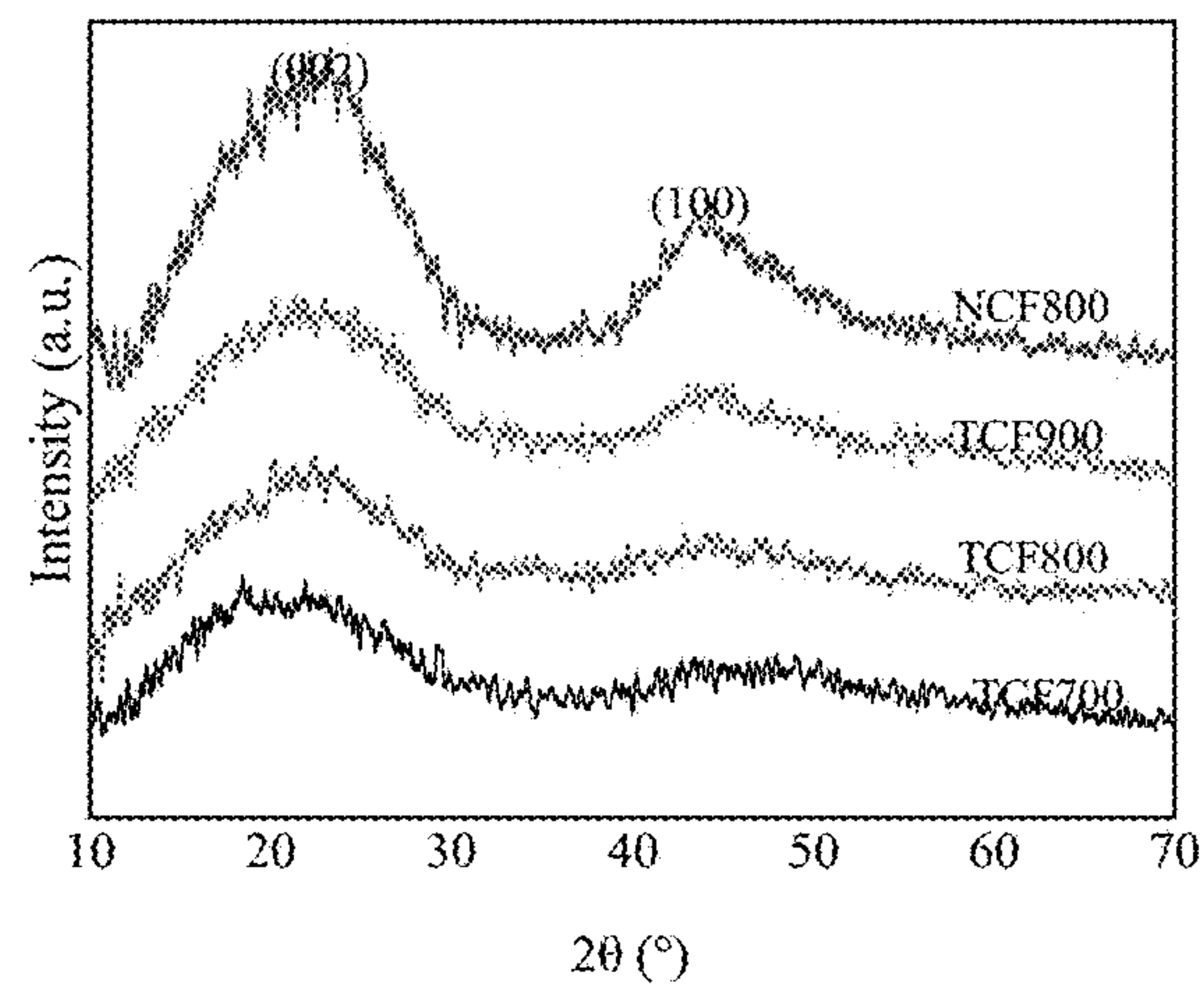


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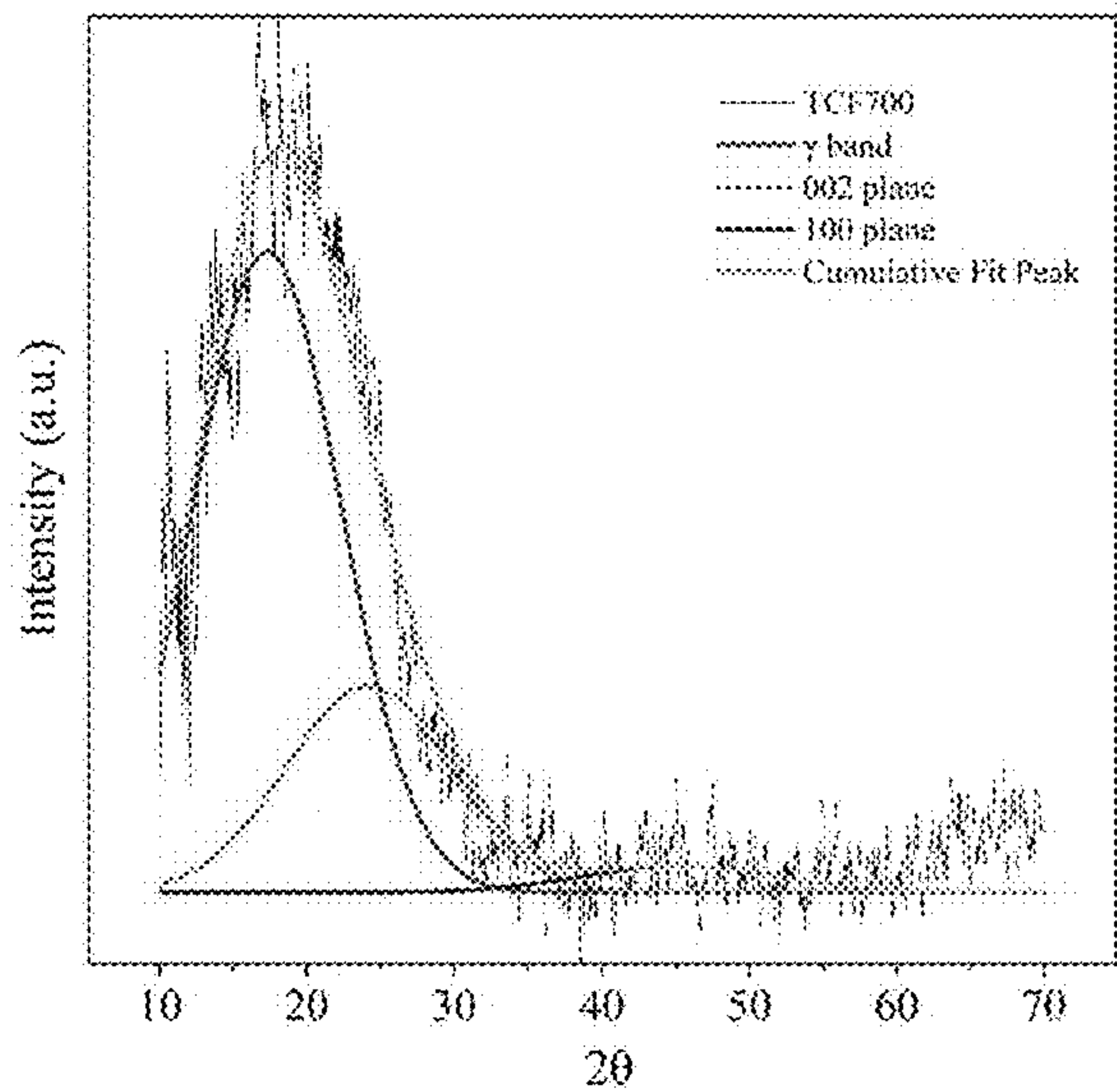


Figure 18A

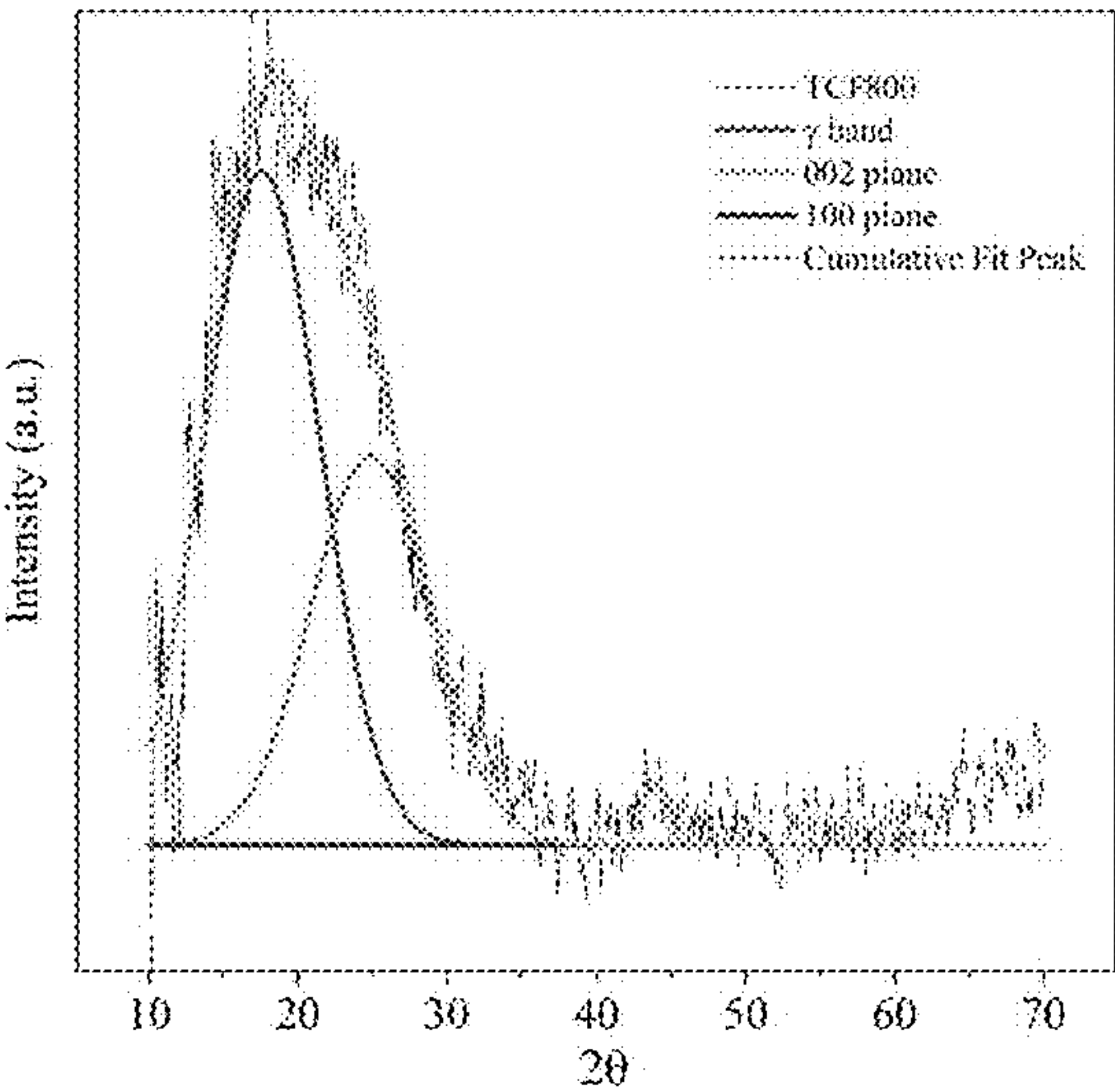


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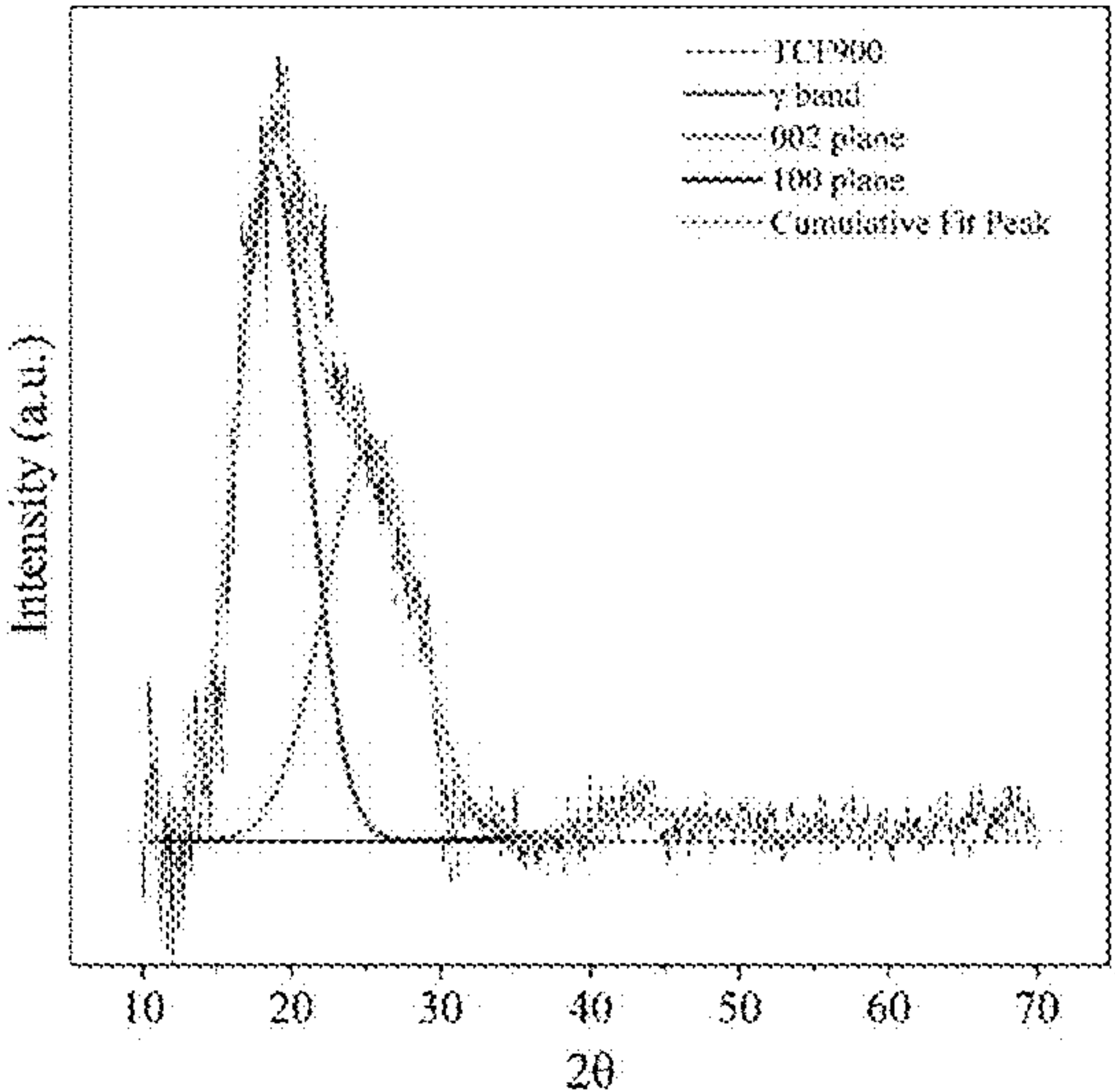


Figure 18C

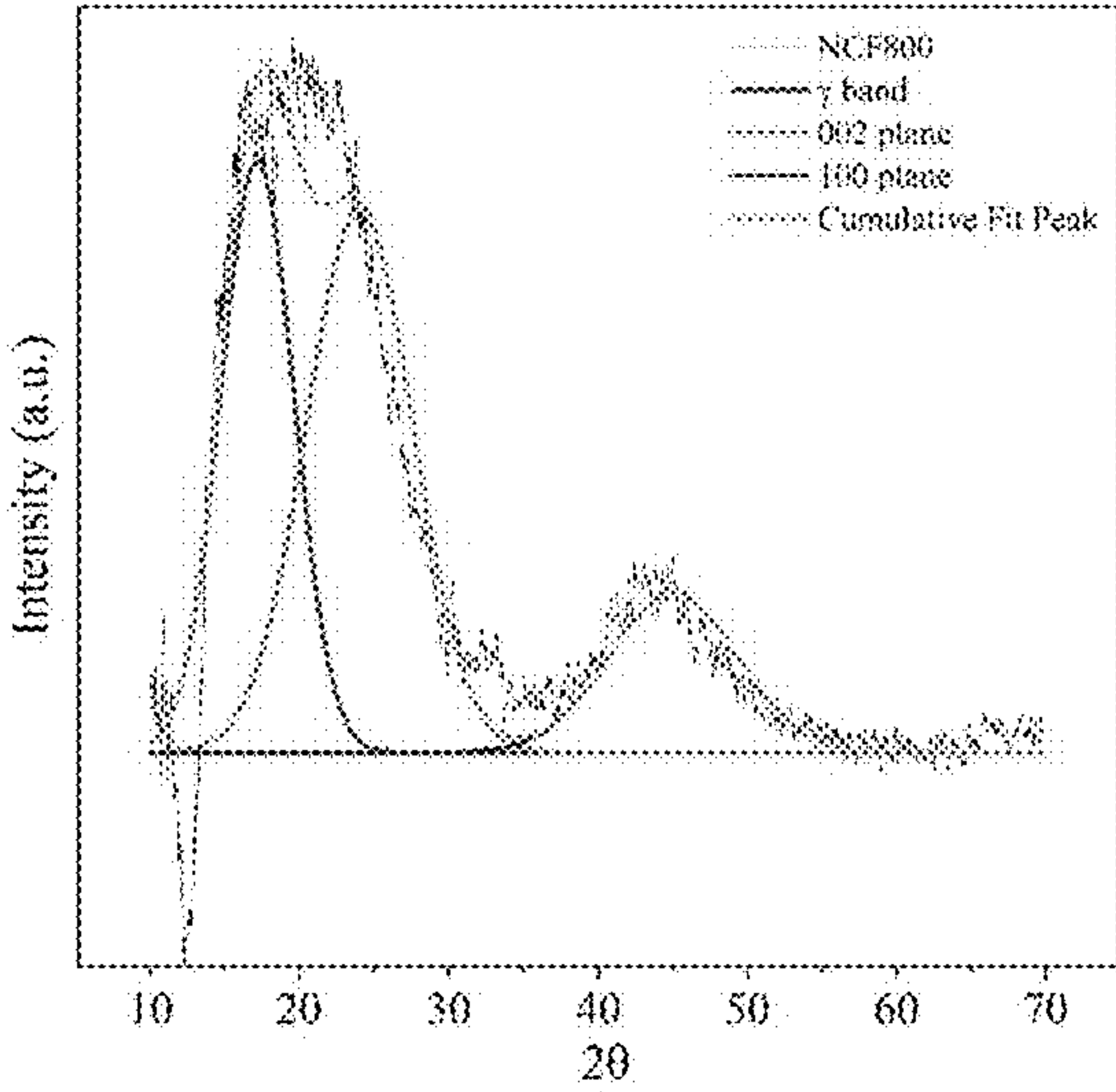


Figure 18D

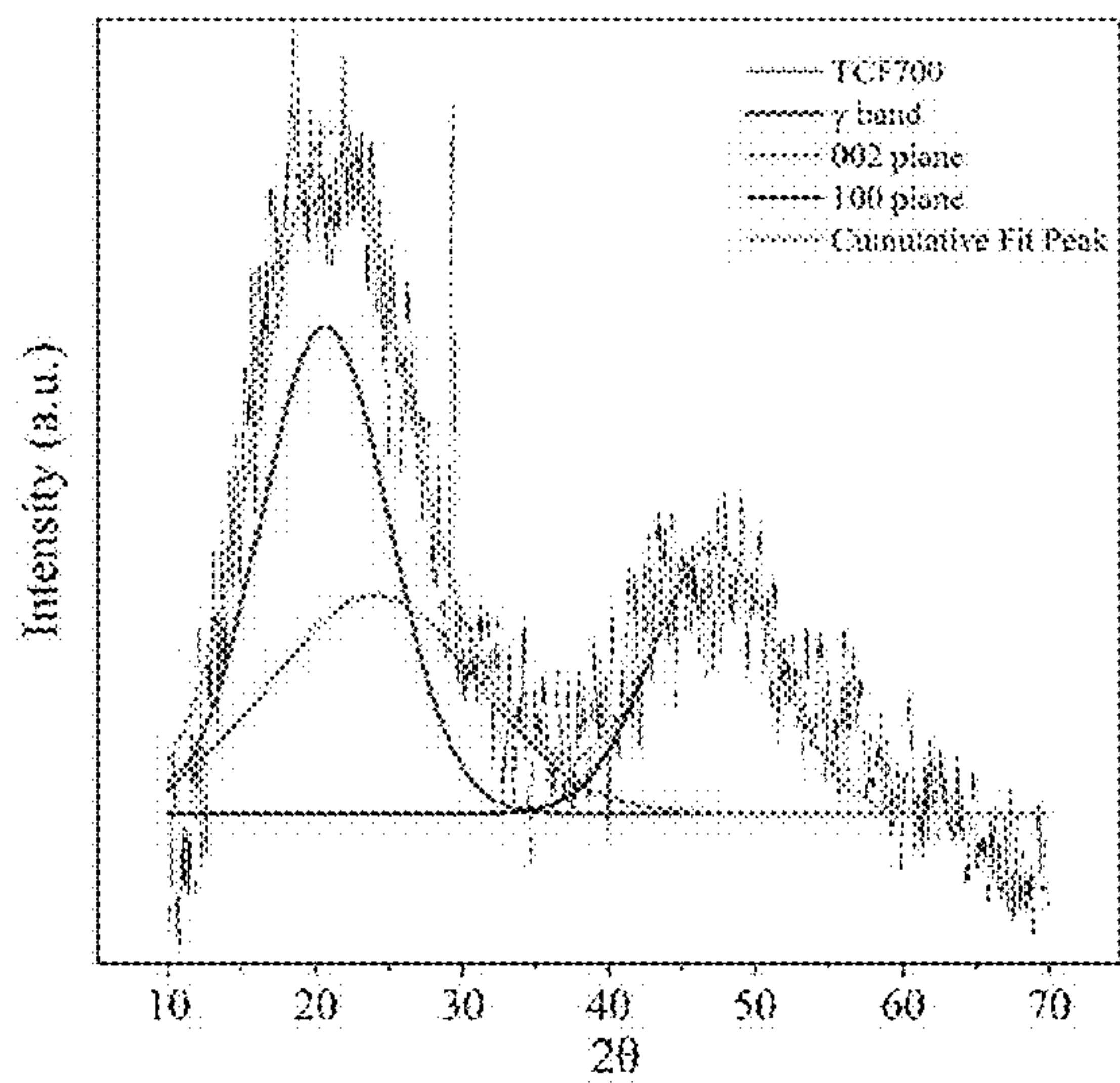


Figure 18E

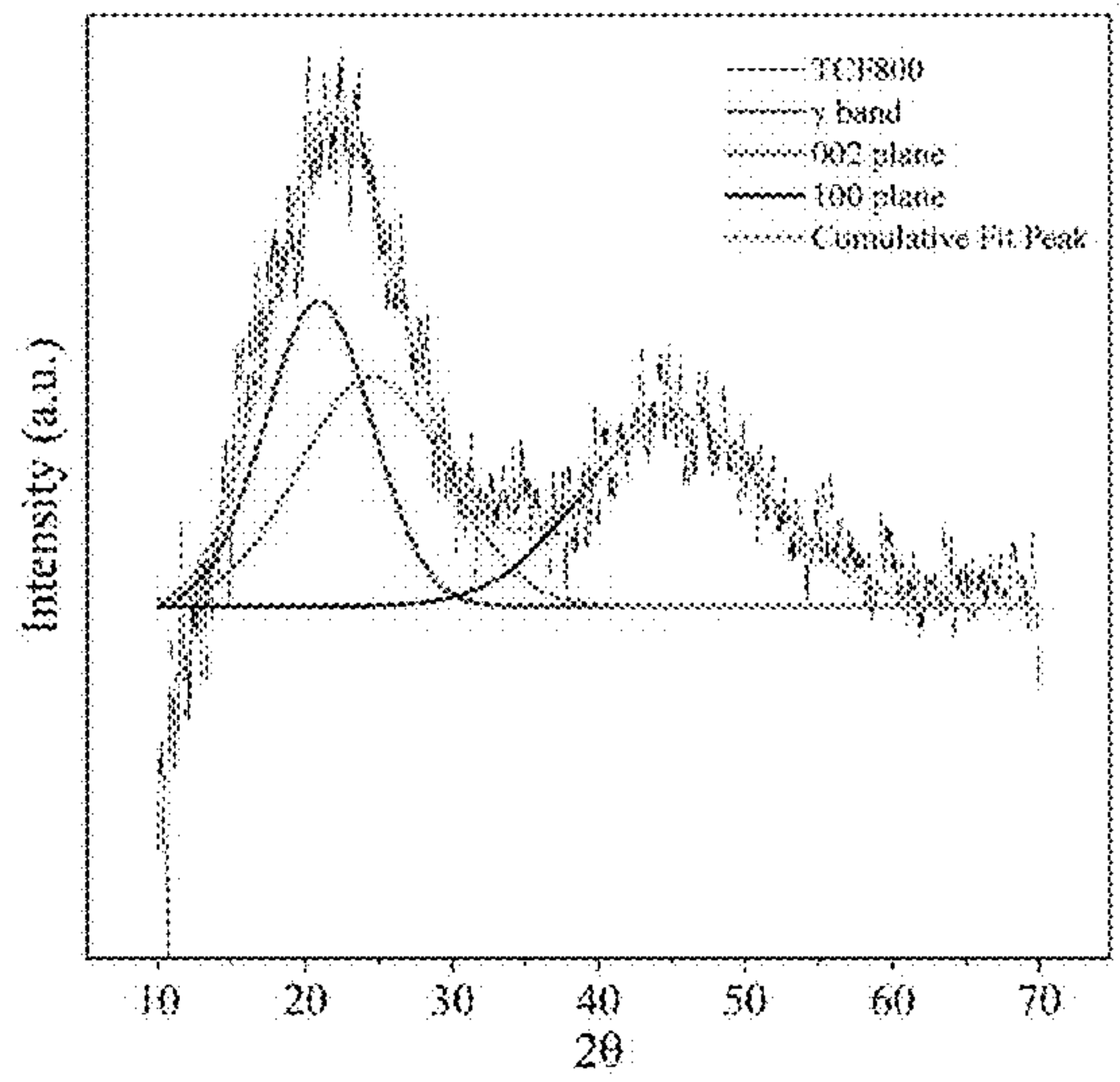


Figure 18F

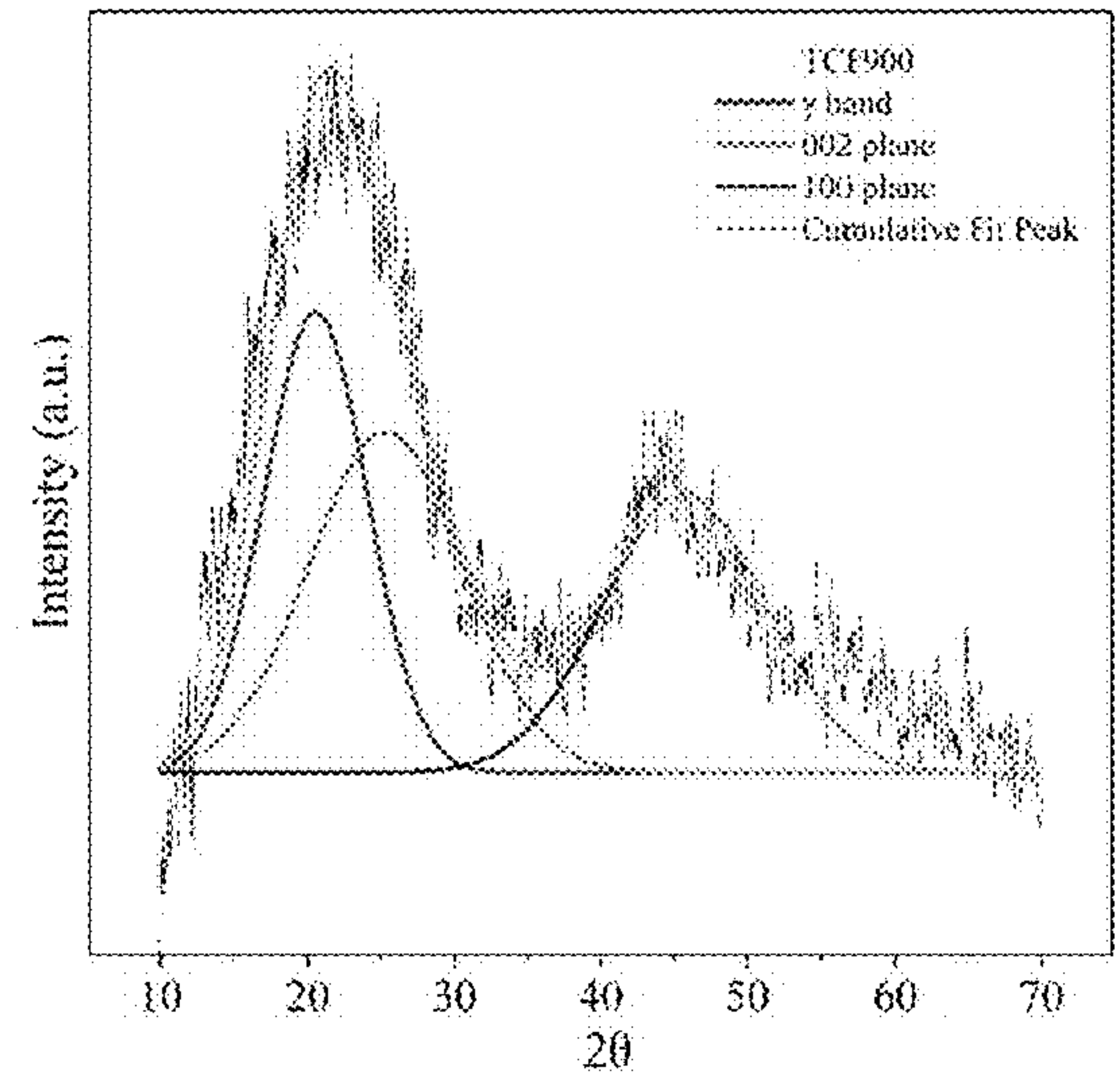


Figure 18G

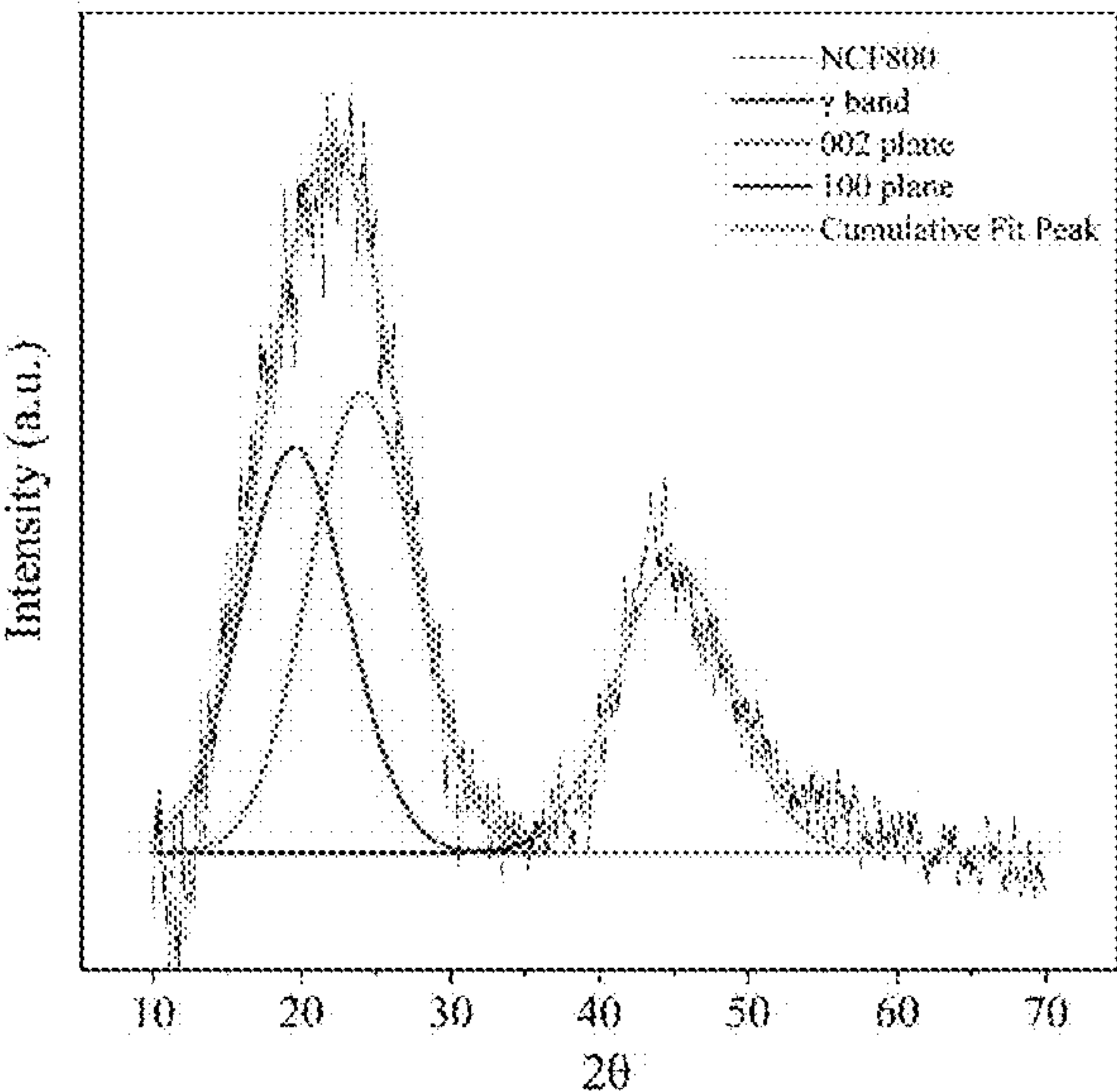


Figure 18H

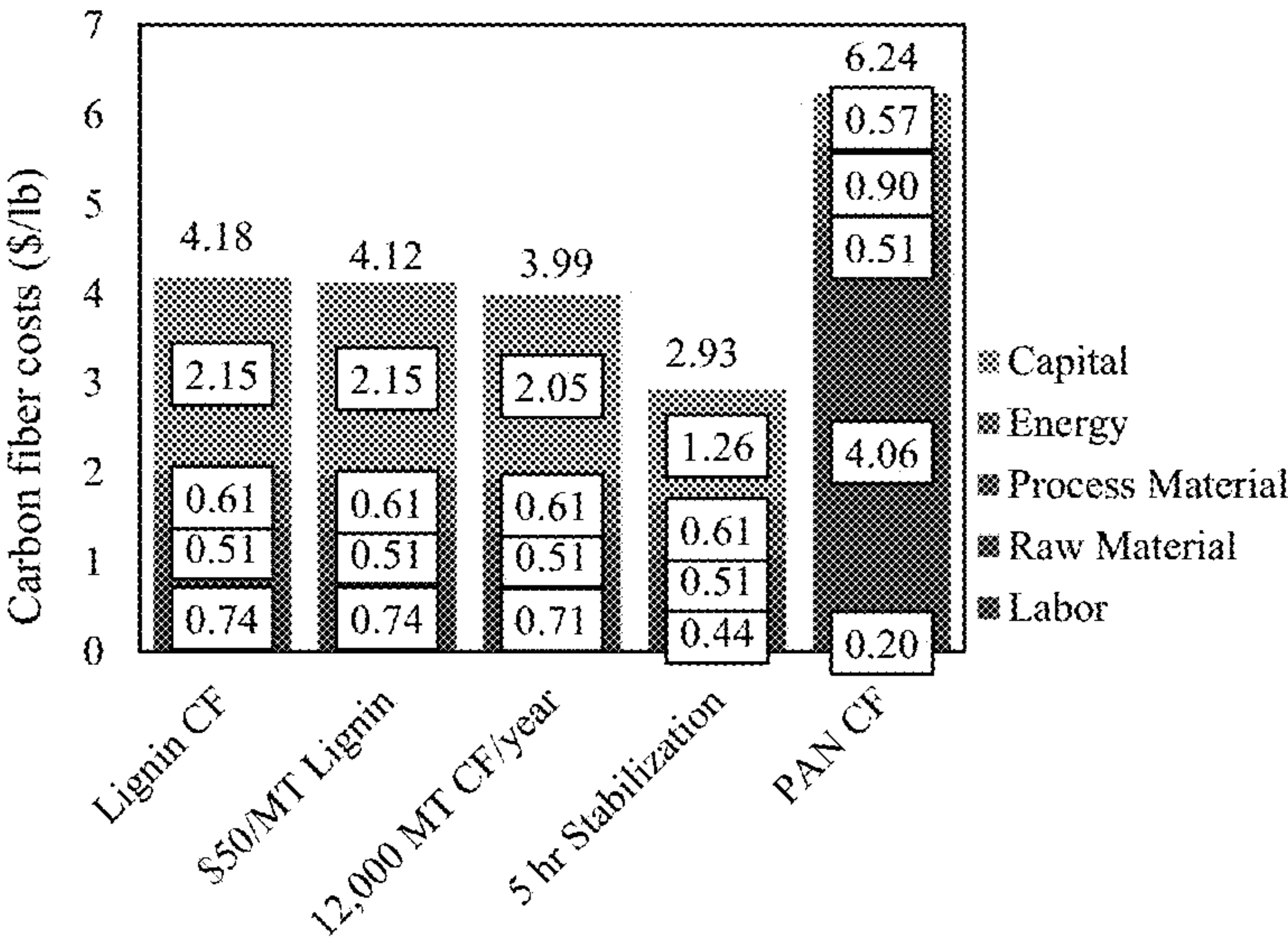


Figure 19

METHOD TO PRODUCE HIGH-QUALITY CARBON FIBER USING LIGNIN

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 63/419,859, filed Oct. 27, 2022, which is hereby incorporated by reference in its entirety.

[0002] This invention was made with government support under PG103393 awarded by U.S. Department of Agriculture/National Institute of Food and Agriculture. The government has certain rights in the invention.

FIELD

[0003] The present application relates to a method to produce high-quality carbon fiber using lignin.

BACKGROUND

[0004] Due to its high strength-to-weight ratio and corrosion resistant nature, carbon fiber composite materials are popular in applications such as aerospace, wind turbine, automobile, sporting goods, and construction industries (Zhang et al., “Unlocking the Response of Lignin Structure for Improved Carbon Fiber Production and Mechanical Strength,” *Green Chem.* 21(18):4981-4987 (2019)). Its utilization is limited by high production cost (Hiremath et al., “Recent Developments in Carbon Fibers and Carbon Nanotube-Based Fibers: A Review,” *Polym. Rev.* 57(2):339-368 (2017)). More than 90% of the global carbon fiber is currently produced from polyacrylonitrile (PAN), a petroleum-derived polymer (Rahaman et al., “A Review of Heat Treatment on Polyacrylonitrile Fiber,” *Polym. Degrad. Stab.* 92(8):1421-1432 (2007)). High costs of carbon fiber are mainly attributed to PAN, which accounts for more than 50% of the production cost (Qu et al., “Potential of Producing Carbon Fiber From Biorefinery Corn Stover Lignin with High Ash Content,” *J. Appl. Polym. Sci.* 135(4):45736 (2017)). Developing cost-competitive carbon fibers using less-costly precursor materials will enable broader applications of carbon fibers. For example, there is a great interest in producing low-cost carbon fibers for automobile industry applications. According to the Department of Energy, lightweight materials could reduce passenger car weight by 50% and improve fuel efficiency by 35% without compromising performance or safety (Energy, U. S. D. of E. (DOE) O. of E. E. and R. E. (EERE). “Carbon Fiber for Lightweight Vehicles,” Summary Report (2013)).

[0005] Lignin has been considered a promising precursor candidate for producing carbon fiber due to its aromatic structure with high fixed carbon, low costs, abundancy, and biorenewable nature (Qu et al., “Potential of Producing Carbon Fiber From Biorefinery Corn Stover Lignin with High Ash Content,” *J. Appl. Polym. Sci.* 135(4):45736 (2017)). In addition to the over 50 million tons of lignin annually produced from paper/pulping industries, lignin is also produced from cellulosic biorefineries as waste streams (Ragauskas et al., “Lignin Valorization: Improving Lignin Processing in the Biorefinery,” *Science* 344(6185):1246843 (2014)). Nonetheless, the use of lignin-based carbon fibers for commercial applications is hindered due to their poor mechanical properties that cannot meet the industrial requirements for structural materials (Li et al., “Molecular Weight and Uniformity Define the Mechanical Performance of Lignin-Based Carbon Fiber,” *J. Mater. Chem. A* 5(25):12740-12746 (2017)).

[0006] The basic steps for producing carbon fibers were similar for different types of precursors in previous studies, which include fiber spinning followed by oxidative thermal stabilization, and carbonization to temperatures of 1000° C. or above with optional graphitization (Salim et al., “The Role of Tension and Temperature for Efficient Carbonization of Polyacrylonitrile Fibers: Toward Low Cost Carbon Fibers,” *Ind. Eng. Chem. Res.* 57(12):4268-4276 (2018)). PAN-based carbon fibers have exceptional tensile properties, attributed to its well-defined and repeated molecular structure. During oxidative stabilization in air, the nitrile polymer converts to a cyclic structure via cyclization, dehydrogenation, aromatization, oxidation, and crosslinking. The newly formed conjugated ladder structure has superior orientation and high thermal stability (Rahaman et al., “A Review of Heat Treatment on Polyacrylonitrile Fiber,” *Polym. Degrad. Stab.* 92(8):1421-1432 (2007)). In the following carbonization process, non-carbon elements are removed with increasing carbonization temperatures. During this process, the cyclic ladder structure of stabilized fibers turns into a well-ordered turbostratic carbon that can achieve high tensile properties. In comparison, lignin is a highly branched, amorphous polyaromatic structure in which single aromatic rings are linked via different types of side chain functional groups without orientation (Nar et al., “Superior Plant Based Carbon Fibers from Electrospun Poly-(Caffeyl Alcohol) Lignin,” *Carbon N. Y.* 103:372-383 (2016)). The structural randomness increases when lignin crosslinks during oxidative stabilization. As a result, lignin-derived carbon fiber has a non-oriented and highly defective structure mostly dominated by amorphous carbons. Since the molecular structure and orientation of a precursor strongly affect mechanical properties of the resultant carbon fibers, various types of lignin obtained from different biomass origins using different lignin isolation methods were used in previous studies to produce carbon fibers (Norberg et al., “A New Method for Stabilizing Softwood Kraft Lignin Fibers for Carbon Fiber Production,” *J. Appl. Polym. Sci.* 128(6):3824-3830 (2013); Culebras et al., “Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors,” *ACS Sustain. Chem. Eng.* 6(7):8816-8825 (2018)). Other than directly processing a purified lignin for fibers, lignin was also physically or chemically modified prior to fiber spinning (Li et al., “Tuning Hydroxyl Groups for Quality Carbon Fiber of Lignin,” *Carbon N. Y.* 139:500-511 (2018); Sudo et al., “A New Modification Method of Exploded Lignin for the Preparation of a Carbon Fiber Precursor,” *J. Appl. Polym. Sci.* 48(8):1485-1491 (1993); Dai et al., “High-Strength Lignin-Based Carbon Fibers via a Low-Energy Method,” *RSC Adv.* 8(3):1218-1224 (2018)). The previous findings showed that using highly purified, solvent-fractionated lignin that have high molecular weights and low polydispersity (Jin et al., “Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance,” *ACS Sustain. Chem. Eng.* 6(11):14135-14142 (2018)), or lignin containing higher concentration of aryl-ether linkages can produce carbon fibers with better mechanical properties compared to their counterpart carbon fibers originated from lignin without the abovementioned characteristics (Hosseinaei et al., “Role of Physicochemical Structure of Organosolv Hardwood and Herbaceous Lignins on Carbon Fiber Performance,” *ACS Sustain. Chem. Eng.* 4(10):5785-5798 (2016)). To date, the highest

mechanical properties of carbon fiber based on a solvent-based spinning of lignin had tensile strength and modulus of up to 1.39 GPa and 98 GPa, respectively. In this study, Kraft lignin was first fractionated using a mixture of acetic acid and water to separate a high molecular weight fraction of lignin which accounts for 1 wt % of the starting lignin. The fractionated lignin solvated in acetic acid and water mixture was then spun into fibers followed by stabilization and carbonization (Jin et al., “Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance,” *ACS Sustain. Chem. Eng.* 6(11): 14135-14142 (2018)). So far, the most effective approach for improving carbon fiber properties has been blending lignin with large amounts of PAN (for example, 1:2 mass ratio of lignin to PAN) followed by wet or gel-spinning the mixtures (Jin et al., “Carbon Fibers Derived from Wet-Spinning of Equi-Component Lignin/Polyacrylonitrile Blends,” *J. Appl. Polym. Sci.* 135(8):1-9 (2018); Demiroglu et al., “Fabrication of Conductive Lignin/PAN Carbon Nanofiber with Enhanced Graphene for the Modified Electrode,” *Carbon N. Y.* 147:262-275 (2019); Liu et al., “Processing, Structure, and Properties of Lignin- and CNT-Incorporated Polyacrylonitrile-Based Carbon Fibers,” *ACS Sustain. Chem. Eng.* 3(9):1943-1954 (2015); Liu et al., “Lignin/Polyacrylonitrile Carbon Fibers: The Effect of Fractionation and Purification on Properties of Derived Carbon Fibers,” *ACS Sustain. Chem. Eng.* 6(7):8554-8562 (2018)). Although tensile strength of the PAN blended carbon fibers in these studies could reach from 1.4 GPa up to 2.47 GPa (Jin et al., “Carbon Fibers Derived from Wet-Spinning of Equi-Component Lignin/Polyacrylonitrile Blends,” *J. Appl. Polym. Sci.* 135(8):1-9 (2018); Liu et al., “Polyacrylonitrile Sheath and Polyacrylonitrile/Lignin Core Bi-Component Carbon Fiber,” *Carbon N. Y.* 149:165-172 (2019)), the improved tensile properties are contributed by PAN. Furthermore, the precursors often contained more PAN than lignin, thus it was difficult to justify them as lignin-based carbon fibers. As an alternative approach, acrylated thermoplastic polymer was synthesized from lignin bio-oil and used as a precursor to produce carbon fibers with tensile strength of 1.7 GPa and tensile modulus of 182 GPa (Luo et al., “Enabling High-Quality Carbon Fiber Through Transforming Lignin Into an Orientable and Melt-Spinnable Polymer,” *J. Clean. Prod.* 307:127252 (2021)), which represent the highest property values could be obtained from a melt-spun lignin-based carbon fibers.

[0007] The present application is directed to overcoming these and other deficiencies in the art.

SUMMARY

[0008] One aspect of the present application relates to a method of producing a lignin-based carbon fiber. This method comprises providing a lignin-containing material, producing a lignin fiber from the lignin-containing material, stabilizing the lignin fiber under tension, where the tension is adjusted during said stabilizing such that the maximum bearable tension is applied to the lignin fiber, and carbonizing the lignin fiber under tension to produce a carbon fiber, where said carbonizing is carried out at a temperature below 1200° C. and where the tension during said carbonizing is adjusted to avoid shrinkage.

[0009] Another aspect of the present application relates to a lignin-based carbon fiber comprising an elemental oxygen content of at least 1 wt %, an elemental carbon content of at

least 65 wt %, an average diameter of about 0.1 μm to about 20 μm , an average tensile strength of from about 2.0 GPa to about 4.0 GPa, and an average tensile modulus of from about 200 GPa to about 400 GPa.

[0010] Another aspect of the present application relates to a molded article for a machine part, electric and electronic part, or automotive part. The article comprises a matrix material and the carbon fiber of the present application dispersed in said matrix material.

[0011] The previous research efforts for the lignin-based carbon fibers have mostly been focused on how to improve precursor quality, mainly in terms of its molecular structure. Noteworthy, chemical structure, physical properties, and rheological properties of a precursor material change significantly during carbon fiber production processes, which eventually leads to changing material properties of resulting fibers. Due to their different precursor properties, there are large variations between physical behaviors of PAN-based and lignin-based fibers. Since PAN decomposes before it melts, solvent dissolved PAN is drawn into fibers and the dissolution solvent is later removed from fiber matrix by water rinsing. PAN fibers are strong and easy to handle, benefited by the high molecular weights and oriented chains in the polymer. During stabilization with fast constant heating rates, PAN fibers are mechanically stretched to reduce fiber diameters, and in the meantime, remove the residue solvent at inner fibers and shrink voids caused by the solvent removal. The applied tension also detangles the fiber polymer chains to enhance a more oriented polymer structure to be oxidized and carbonized. In comparison, either melt spinning or solvent-based spinning method can be used to draw lignin fiber depending on glass transition temperature of a given lignin. However, lignin fibers are much more difficult to handle than PAN or other precursors derived fibers, because, as-spun fiber of lignin is usually very brittle and weak due to its poor structural orientation and uniformity. During stabilization processing, lignin can soften and its fiber viscosity is highly sensitive to increasing temperature. Due to decreasing viscosity, fibers can fuse or even melt back to a non-fiber form. Therefore, lignin fibers were usually heated slowly in an oxygen environment to increase crosslinking, which can increase glass transition temperature of lignin to produce structurally-highly restricted, non-fusible fibers. Due to the weak fibers and low fiber viscosity, stretching fibers was absent for most of lignin fibers in previous studies, except only a few studies could apply tension to reduce fiber diameters (Liu et al., “Polyacrylonitrile Sheath and Polyacrylonitrile/Lignin Core Bi-Component Carbon Fiber,” *Carbon N. Y.* 149:165-172 (2019); Norberg et al., “A New Method for Stabilizing Softwood Kraft Lignin Fibers for Carbon Fiber Production,” *J. Appl. Polym. Sci.* 128(6):3824-3830 (2013); Hosseinaei et al., “Role of Physicochemical Structure of Organosolv Hardwood and Herbaceous Lignins on Carbon Fiber Performance,” *ACS Sustain. Chem. Eng.* 4(10):5785-5798 (2016); Mainka et al., “Characterization of the Major Reactions During Conversion of Lignin to Carbon Fiber,” *J. Mater. Res. Technol.* 4(4):377-391 (2015); Jin et al., “Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance,” *ACS Sustain. Chem. Eng.* 6(11):14135-14142 (2018), which are hereby incorporated by reference in their entirety).

[0012] Considering significant chemical reactions and physical material structural changes occur during fiber fab-

rication processes, a research area that has been largely overlooked is examine whether it is possible to control lignin transformation via controlling processing conditions of lignin fibers for producing carbon fiber. In the present application, lignin's material chemistry was manipulated by developing temperature and tension coupled profiles to control lignin transformation during stabilization and carbonization processes of lignin fibers. Based on the lignin-tailored, controlled production process, carbon fibers with unprecedentedly high tensile properties meeting commercial grade requirements were obtained from a melt-spun lignin in the absence of additives or chemical treatment of lignin using unconventionally low carbonization temperatures.

[0013] Producing low-cost carbon fibers is of great interest for automobiles and any other industries that can benefit from non-corrosive, lightweight materials with high tensile properties. Although lignin has been considered a candidate precursor for low-cost carbon fibers, the major obstacle is the poor mechanical properties of resultant carbon fibers that are far lower than the commercial grade requirements. For the first time, lignin-based carbon fiber with commercial grade properties was produced without using any additives or chemical modifications. The carbon fiber produced from a melt-spun lignin fiber using a carbonization temperature of 700° C. achieved an average tensile strength of 2.33 GPa and tensile modulus of 209 GPa with the maximum tensile strength of 3.77 GPa and modulus of 273 GPa. The unprecedentedly high mechanical properties described in the present application are attributed to the development of a fiber processing method specifically tailored to control lignin physiochemistry. This application describes how controlling fiber processing conditions can affect the interrelationships between physical and chemical structures of lignin-based fibers and therefore improve mechanical properties of carbon fibers. These studies showed that by using heating and tension profiles with adjusted heating rate and tension stress during stabilization, it is possible to control lignin bond cleavages and facilitates molecular rearrangement to transform lignin structure into an oriented molecular structure with reduced random crosslinking and stronger inter-unit linkage. When fiber axial shrinkage was prohibited during subsequent carbonization by controlling tension and heating rate, the stabilized fibers could easily be cyclized and graphitized using very low temperatures to form a well aligned structure in which amorphous and turbostratic carbons are connected by strong alkyl linkages. Overall, the work described in the present application shows the ability to overcome intrinsic defects in lignin molecules through controlling processing conditions of fibers, thereby producing carbon fiber with significantly improved mechanical properties. These results open a door for producing green low-cost carbon fibers for industrial applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIGS. 1A-1D are images showing melt-spun fibers for stabilization. FIG. 1A shows as-spun fiber (AF) spool. FIG. 1B shows AF fiber bundles prepared for stabilization.

[0015] FIGS. 1C-1D show weights that are attached to stretch the spun fibers during stabilization.

[0016] FIGS. 2A-2C show Raman analysis results of CFs: cross-section view spectra (FIG. 2A); top view spectra (FIG. 2B); and I_D/I_G ratios (FIG. 2C) of CFs in different fiber directions after Gaussian fitting.

[0017] FIG. 3 shows Small-Angle X-Ray Scattering (SAXS) results of CFs.

[0018] FIGS. 4A-4C show heating profiles and tension adjustments of spun fibers during stabilization: softwood organosolv (OL) (FIG. 4A); 90/10 softwood organosolv/softwood Indulin kraft lignin (OL/KL) (FIG. 4B); and 80/20 OL/KL (FIG. 4C). Grey triangles indicate when the weight loading applied to the fibers was adjusted. Weight loading remained constant until the next adjustment. The tension stress of fibers was measured only when the weight loading was adjusted. Due to decreasing fiber diameters during stabilization, tension stress per fiber is expected to increase even with the same weight loading.

[0019] FIGS. 5A-5B are images showing stabilized fiber before carbonization (FIG. 5A) and after carbonization (FIG. 5B) using a constant heating rate of 7° C./min. Bent graphene sheet and broken fibers resulted from carbonizing stabilized fibers caused by excessive fiber shrinkage.

[0020] FIGS. 6A-6D show Scanning Electron Microscopy (SEM) images of representative CFs.

[0021] FIG. 7 is a graph showing stress-strain curve.

[0022] FIGS. 8A-8B show tensile strength (FIG. 8A) and tensile modulus (FIG. 8B) of carbon fibers (CFs) produced using different processing conditions.

[0023] FIGS. 9A-9F are transmission electron microscopy (TEM) images of CFs: NCF700 (FIG. 9A); NCF1000 (FIG. 9B); TCF700 (FIG. 9C); TCF800 (FIG. 9D); TCF900 (FIG. 9E); and TCF1000 (FIG. 9F).

[0024] FIGS. 10A-10H show heteronuclear-single-quantum-coherence nuclear magnetic resonance (HSQC-NMR) spectra of raw lignin, as-spun fiber (AF) and stabilized fiber (SF). FIGS. 10A-10B show HSQC-NMR spectra of raw lignin. FIGS. 10C-10D show HSQC-NMR spectra of AF. FIGS. 10E-10F show HSQC-NMR spectra of NSF stabilized up to 165° C. FIGS. 10G-10H show HSQC-NMR spectra of TSF stabilized up to 165° C. FIGS. 10A, 10C, 10E, and 10G show oxygen and aromatic-related regions. FIGS. 10B, 10D, 10F, and 10H show non-oxygen aliphatic regions. FIG. 10I shows the structures of compounds β -aryl ether (β -O-4), phenyl coumaran (β -5), Resinol (B-B), secoisolariciresinol, guaiacyl hydroxyethyl ketone, guaiacyl propanol, guaiacol, syringyl, ferulate, and stilbene.

[0025] FIG. 11 shows Fourier Transform Infrared (FTIR) spectra of SFs: 1 (3100-3600 cm^{-1}) for OH; 2 (2948 cm^{-1}) and 3 (2850 cm^{-1}) for alkyl C—H; 4 (1850 cm^{-1}); 5 (1750 cm^{-1}) and 6 (1700 cm^{-1}) for C=O; 7 (1600 cm^{-1}) and 8 (1500 cm^{-1}) for aromatic ring vibration; and 9 (1232 cm^{-1}) and 10 (1032 cm^{-1}) for C—O stretch.

[0026] FIG. 12 shows pyrolysis-GC/MS chromatogram of AF, NSF, and TSF.

[0027] FIGS. 13A-13B show Raman spectra of SFs measured from cross-section view (FIG. 13A) and top view (FIG. 13B).

[0028] FIG. 14 shows FTIR spectra of CFs: 1 (2914 cm^{-1}) and 2 (2850 cm^{-1}) for alkyl C—H stretch; 3 (1760 cm^{-1}) and 4 (1650 cm^{-1}) for C=O; and 5 (1500 cm^{-1}), 6 (913 cm^{-1}), and 7 (833 cm^{-1}) for aromatic ring vibration.

[0029] FIGS. 15A-15D show Gaussian fitting of X-ray photoelectron spectroscopy (XPS) spectra of CFs: CF700 (FIG. 15A); TCF800 (FIG. 15B); TCF900 (FIG. 15C); NCF800 (FIG. 15D). Where 284.8 eV, 286.3 eV, 288.0 eV, and 289.1 eV represent —C—C—/—C—H—; —C—O—; —C=O; and —O—C=O, respectively.

[0030] FIGS. 16A-16L show Gaussian fitting of Raman spectra of CFs. FIGS. 16A-16F show the cross-section view spectra: TCF600 (FIG. 16A); TCF700 (FIG. 16B); TCF800 (FIG. 16C); TCF900 (FIG. 16D); PCF800 (FIG. 16E); NCF800 (FIG. 16F). FIGS. 16G-16L show the top view spectra: TCF600 (FIG. 16G); TCF700 (FIG. 16H); TCF800 (FIG. 16I); TCF900 (FIG. 16J); PCF800 (FIG. 16K); NCF800 (FIG. 16L).

[0031] FIGS. 17A-17B show X-ray diffraction (XRD) equatorial scans measured parallel (FIG. 17A) and perpendicular (FIG. 17B) to the fiber axis.

[0032] FIGS. 18A-18H show Gaussian fitting of XRD spectra of various CFs. FIGS. 18A-18D show the parallel scan spectra: TCF700 (FIG. 18A); TCF800 (FIG. 18B); TCF900 (FIG. 18C); NCF800 (FIG. 18D). FIGS. 18E-18H show the perpendicular scan spectra: TCF700 (FIG. 18E); TCF800 (FIG. 18F); TCF900 (FIG. 18G); NCF800 (FIG. 18H).

[0033] FIG. 19 is a bar graph showing comparison of current and projected production costs of lignin-based CF based on this work to literature-estimated PAN-based CF production cost.

DETAILED DESCRIPTION

[0034] One aspect of the present application relates to a method of producing a lignin-based carbon fiber. This method comprises providing a lignin-containing material, producing a lignin fiber from the lignin-containing material, stabilizing the lignin fiber under tension, where the tension is adjusted during said stabilizing such that the maximum bearable tension is applied to the lignin fiber, and carbonizing the lignin fiber under tension to produce a carbon fiber, where said carbonizing is carried out at a temperature below 1200° C. and where the tension during said carbonizing is adjusted to avoid shrinkage.

[0035] Any lignin-containing material can be used to produce the lignin-based carbon fiber of the present application. Suitable lignin-containing materials that can be used may include, but are not limited to, hardwoods (e.g., balsa wood, beech, ash, birch, Brazil wood, cherry, chestnut, elm, hickory, mahogany, maple, oak, rosewood, teak, walnut, locust, mango, alder, and the like), softwoods (e.g., pine, southern pine, fir, spruce, cedar, hemlock, and the like), cotton stalk, jute, flax fibers, hemp, sisal, bind, rattan, agave, coconut coir, grass, wheat stalk, rice stalk, barley straw, rye straw, wheat straw, rice straw, hemp stalks, kenaf stalks, sugar cane residue, bamboo, cork, and the like, and any combination thereof.

[0036] In some embodiments, the lignin-containing material is a combination of two or more lignin-containing materials, three or more lignin-containing materials, four or more lignin-containing materials, five or more lignin-containing materials, six or more lignin-containing materials, seven or more lignin-containing materials, eight or more lignin-containing materials, nine or more lignin-containing materials, or ten or more lignin-containing materials.

[0037] In some embodiments, the lignin-containing material is used in combination with one or more polymers. Suitable polymers that can be used include non-lignin polymers, such as cellulose, polyacrylonitrile (PAN), and polyethylene terephthalate (PET).

[0038] In some embodiments, the lignin-containing material is used in combination with one or more modified lignins.

[0039] In one embodiment, the lignin-containing material is a softwood lignin. Suitable softwood lignin that can be used include 100% softwood organosolv lignin, 100% softwood kraft lignin, or combinations thereof.

[0040] In some embodiments, the lignin-containing material is a combination of two or more softwood lignins, three or more softwood lignins, four or more softwood lignins, five or more softwood lignins, six or more softwood lignins, seven or more softwood lignins, eight or more softwood lignins, nine or more softwood lignins, or ten or more softwood lignins.

[0041] If a combination of several lignin-containing materials is used, each lignin-containing material can be present in the amount of from about 0.01 wt % to about 99.99 wt %, from about 0.1 wt % to about 99.9 wt %, from about 1 wt % to about 99 wt %, from about 2 wt % to about 98 wt %, from about 3 wt % to about 97 wt %, from about 4 wt % to about 96 wt %, from about 5 wt % to about 95 wt %, from about 6 wt % to about 94 wt %, from about 7 wt % to about 93 wt %, from about 8 wt % to about 92 wt %, from about 9 wt % to about 91 wt %, from about 10 wt % to about 90 wt %, from about 15 wt % to about 85 wt %, from about 20 wt % to about 80 wt %, from about 25 wt % to about 75 wt %, from about 30 wt % to about 70 wt %, from about 35 wt % to about 65 wt %, from about 40 wt % to about 60 wt %, from about 0.01 wt % to about 50 wt %, from about 0.1 wt % to about 50 wt %, from about 1 wt % to about 40 wt %, from about 2 wt % to about 30 wt %, from about 3 wt % to about 20 wt %, from about 1 wt % to about 10 wt %, from about 2 wt % to about 10 wt %, from about 3 wt % to about 10 wt %, from about 4 wt % to about 10 wt %, from about 5 wt % to about 10 wt %, from about 6 wt % to about 10 wt %, from about 7 wt % to about 10 wt %, or from about 8 wt % to about 10 wt %.

[0042] In some embodiments, the lignin-containing material is a mixture of softwood Kraft lignin and softwood organosolv lignin. For example, the lignin-containing material is a mixture of softwood Kraft lignin and softwood organosolv lignin, where the softwood Kraft lignin is present in the amount of from about 0.01 wt % to about 99.99 wt %, from about 0.1 wt % to about 99.9 wt %, from about 1 wt % to about 99 wt %, from about 2 wt % to about 98 wt %, from about 3 wt % to about 97 wt %, from about 4 wt % to about 96 wt %, from about 5 wt % to about 95 wt %, from about 6 wt % to about 94 wt %, from about 7 wt % to about 93 wt %, from about 8 wt % to about 92 wt %, from about 9 wt % to about 91 wt %, from about 10 wt % to about 90 wt %, from about 15 wt % to about 85 wt %, from about 20 wt % to about 80 wt %, from about 25 wt % to about 75 wt %, from about 30 wt % to about 70 wt %, from about 35 wt % to about 65 wt %, from about 40 wt % to about 60 wt %, from about 0.01 wt % to about 50 wt %, from about 0.1 wt % to about 50 wt %, from about 1 wt % to about 40 wt %, from about 2 wt % to about 30 wt %, from about 3 wt % to about 20 wt %, from about 1 wt % to about 10 wt %, from about 2 wt % to about 10 wt %, from about 3 wt % to about 10 wt %, from about 4 wt % to about 10 wt %, from about 5 wt % to about 10 wt %, from about 6 wt % to about 10 wt %, from about 7 wt % to about 10 wt %, or from about 8 wt % to about 10 wt % and softwood organosolv lignin is present in the amount of from about 0.01 wt % to about 99.99 wt %, from about 0.1 wt % to about 99.9 wt %, from about 1 wt % to about 99 wt %, from about 2 wt % to about 98 wt %, from about 3 wt % to about 97 wt %, from about

4 wt % to about 96 wt %, from about 5 wt % to about 95 wt %, from about 6 wt % to about 94 wt %, from about 7 wt % to about 93 wt %, from about 8 wt % to about 92 wt %, from about 9 wt % to about 91 wt %, from about 10 wt % to about 90 wt %, from about 15 wt % to about 85 wt %, from about 20 wt % to about 80 wt %, from about 25 wt % to about 75 wt %, from about 30 wt % to about 70 wt %, from about 35 wt % to about 65 wt %, from about 40 wt % to about 60 wt %, from about 0.01 wt % to about 50 wt %, from about 0.1 wt % to about 50 wt %, from about 1 wt % to about 40 wt %, from about 2 wt % to about 30 wt %, from about 3 wt % to about 20 wt %, from about 1 wt % to about 10 wt %, from about 2 wt % to about 10 wt %, from about 3 wt % to about 10 wt %, from about 4 wt % to about 10 wt %, from about 5 wt % to about 10 wt %, from about 6 wt % to about 10 wt %, from about 7 wt % to about 10 wt %, or from about 8 wt % to about 10 wt %.

[0043] Lignin can be chemically or physically pretreated before spinning in order to purify lignin containing material or increase spinnability of the lignin containing material. Suitable pretreatment conditions that can be used include, but are not limited to, acetylation and/or solvent fractionation.

[0044] In one embodiment, the method further includes the step of purifying the lignin-containing material before the lignin fiber is produced.

[0045] Lignin features can vary greatly based on the biomass species, the extraction method, batch differences, purification steps, and storage duration. One important lignin parameter is its inorganic impurities. Usually, impurities are due to either the lignin extraction process or the growth environment of plants (nutritional and functional minerals). Identifiable elements in these impurities include Na, K, Ca, Mg, Al, Si, Fe, P, S, Mn, and Cu. These impurities are converted into metallic oxides and other inorganic salts under high temperature during carbonization and preserved as “ash” in the final products. The presence of ash has at least two drawbacks. First, it interrupts the consistency of the carbon structure, thus resulting in carbon fibers with structural defects. Second, the inorganic impurities can act as a catalyst to accelerate the decomposition of lignin, which will eventually lead to a low carbon yield and introduce more defects in the carbon fiber structure. In most cases, inorganic impurities can be removed through effective purification methods. Polysaccharides, and other impurities such as solid particles can be removed through fractionation.

[0046] Suitable techniques that can be used to purify lignin-containing material include washing, such as water washing or acid washing; fractionation, such as alcohol (methanol) fractionation, aqueous acetone fractionation, pH-fractionation, hot acetic acid-water fractionation; ultrafiltration; and solvent extraction.

[0047] Lignin fibers can be prepared from the lignin-containing material by spinning, melt-blow, phase inversion extrusion (e.g., wet-spinning, dry-spinning, gel-spinning, melt spinning, and electro-spinning) and other methods.

[0048] One embodiment relates to the method of the present application where the step of producing a lignin fiber is carried out by spinning the lignin-containing material.

[0049] Fiber spinning techniques that are widely used in the production of fibers generally include conventional spinning techniques (such as melt spinning, wet spinning, dry spinning, and gel spinning), as well as electrospinning and centrifugal spinning. Conventional fiber spinning tech-

niques often yield polymeric fibers with diameters in the micrometer range. Electrospinning and centrifugal spinning are capable of consistently producing fibers with diameters down to several nanometers.

[0050] Solution spinning is used to spin fibers from solutions of the dissolved polymer. It can be divided into three spinning techniques, dry spinning, wet spinning, and gel spinning, which all involve the preparation of homogenous spinning dopes. Solution-spun fibers generally have better mechanical performance than melt-spun fibers mainly due to the higher draw ratio of fibers.

[0051] According to the present application, the lignin-containing material can be spun using melt-spinning, wet-spinning, dry-spinning, gel-spinning techniques, or electro-spinning.

[0052] Melt-spinning of lignin or lignin-containing material is a technique that has been frequently used to prepare lignin or lignin-containing fibers due to its low cost and scalability. The excessively high melt-spinning temperatures should be avoided to prevent volatile formation during melt-spinning. These volatiles can result in flaws and pores in the fibers and can be detrimental to the quality of lignin-based carbon fibers. A mass loss lower than 5% at the spinning temperature is considered to be essential for yielding fine fibers. During the melt-spinning process, it is preferable to melt-spin lignin or lignin-containing material at relatively low temperatures to eliminate the occurrence of decomposition and pre-mature crosslinking reactions. The mechanical properties of melt-spun lignin fibers mainly depend on different factors such as the source of lignin (molecular weight, softening temperature, molecular structure), degree of crystallinity, and orientation of the fiber, which are closely related to processing parameters of the melt spinning process (i.e., heating temperature, extrusion speed, take-up speed, etc.)

[0053] Wet-spinning is an alternative spinning method that can be used to prepare lignin or lignin-containing fibers. Compared to melt-spinning, wet-spinning does not require that lignins possess certain thermal properties; instead, it requires lignins to be soluble in a particular solvent. Suitable solvents that can be used for wet-spinning include dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and other similar solvents. Due to lignin's low MW and low viscosity in solution, it is usually wet-spun in the presence of other polymers, such as PAN.

[0054] Dry-spinning is less commonly used for lignin spinning. Compared with wet-spinning, dry-spinning requires that lignin or lignin-containing material be dissolved in a much more volatile solvent, and then the fiber can be spun while the dope passes through hot air. Diffusion issues in coagulant baths that occur during wet-spinning do not apply, but good control of the solvent evaporation rate is necessary. Suitable solvents that can be used for dry-spinning of lignin or lignin-containing material include acetone, dimethylformamide (DMF), and other similar solvents. During the dry-spinning, temperatures higher than 25° C. must be applied to effectively evaporate air.

[0055] Gel spinning is a recently developed fiber spinning technique for producing lignin-based high-performance fibers. This process is similar to wet spinning. The hot polymer solution is extruded through a spinneret into an air gap, before being placed into a cooling coagulation bath to form as-spun gel filaments. The resulting as-spun gel fibers are collected onto a rotating winder and later immersed in

the coagulation bath for a certain duration of time. The fibers then pass through the air oven or hot oil, where they are heated and stretched to form high-performance solid fibers. Typically, gel-spun fibers have higher draw ratios than fibers processed by other fiber spinning techniques. This is because the lower chain entanglements and remaining solvents in the gel structure promote chain stretching in the drawing process. Lignin is mainly blended with PAN or PVA, which are common polymers used in gel-spun fibers. Several factors that influence the mechanical performance of gel-spun lignin-based fibers should be taken into consideration. For instance, polymer molecular weight, polymer concentration, and solvent removal may affect fiber spinnability and fiber microstructure. Other factors such as the coagulation temperature, spinning dopes, coagulation solvent compositions, and fiber gelation time also impact the strength of gel-spun fibers.

[0056] Electrospinning involves an electrohydrodynamic process, during which a liquid droplet is electrified to generate a jet, followed by stretching and elongation to generate fibers. During electrospinning, the polymer dope with a certain viscosity is extruded through the spinneret by the pump and forms a spherically shaped droplet to decrease the surface free energy. The final properties and morphologies of electrospun lignin fibers are largely affected by the solution properties, electrospinning conditions and the surrounding environment, including viscosity, conductivity and surface tension of spinning dope, applied voltage, distance of the spinneret from the target substrate, injection rate, temperature, humidity and solvent volatility.

[0057] The lignin-containing material can be spun at a temperature from about -150°C . to about 300°C ., from about -100°C . to about 300°C ., from about -90°C . to about 250°C ., from about -80°C . to about 250°C ., from about -70°C . to about 250°C ., from about -60°C . to about 250°C ., from about -50°C . to about 250°C ., from about -40°C . to about 250°C ., from about -30°C . to about 250°C ., from about -20°C . to about 250°C ., from about -10°C . to about 250°C ., from about 0°C . to about 250°C ., from about 10°C . to about 250°C ., from about 20°C . to about 250°C ., from about 30°C . to about 250°C ., from about 40°C . to about 250°C ., from about 50°C . to about 250°C ., from about 60°C . to about 250°C ., from about 70°C . to about 250°C ., from about 80°C . to about 250°C ., from about 90°C . to about 250°C ., from about 100°C . to about 250°C ., from about -100°C . to about 300°C ., from about -100°C . to about 250°C ., from about -100°C . to about 200°C ., or from about -100°C . to about 150°C .

[0058] Adjustable parameters in the stabilization of the lignin-based carbon fiber include, but not limited to, the heating rate, the stabilization temperature, tension stress, and the stabilization environment.

[0059] According to the present application, the lignin fiber can be stabilized in an oxidative or inert environment. In one embodiment, the lignin fiber is stabilized in an inert environment. For example, the lignin fiber can be stabilized under argon, nitrogen, helium, neon, krypton, and/or xenon atmosphere. In another embodiment, the lignin fiber is stabilized in an oxidative environment. For example, the lignin fiber can be stabilized in air, oxygen, ozone, or HCl/air.

[0060] According to the present application, while the lignin fiber is being stabilized, the tension applied to the lignin fiber is being adjusted. The amount of tension loading

is adjusted to not only to ensure the fiber is stretched to obtain a thin stabilized fiber, but the fiber also is placed under high tension force throughout the entire stabilization process (which will tune lignin chemistry during stabilization). In the meantime, caution should be paid not to overload tension to break fibers. In the initial stage of stabilization, the fiber is usually stretchable but very weak. As stabilization temperature and/or stabilization time increase, the glass transition temperature (T_g) increases, and the fiber hardens. As a result, the fibers at later stages of the stabilization are stronger than initial fiber but more difficult to stretch.

[0061] At temperatures near to the softening points of lignin, decreasing fiber viscosity is highly sensitive to increasing temperature and the weak fibers can easily break when stretched. Thus, low heating rates and small tension are applied at the beginning of the stabilization process. The fibers at this temperature range could be stretched using a small tension to reduce fiber diameters. Once the fiber becomes partially stabilized, higher heating rates are applied to these partially stabilized fibers because the fibers became less fusible and stronger than the initial fibers. The partially stabilized fibers are also difficult to stretch and can even shrink in the fiber direction. Thus, tension loading has to be increased to prevent fiber shrinkage and to continue stretching the fibers. Thus, for the same precursor fiber, smaller amounts of tension loading are applied initially at low stabilization temperatures to stretch fibers and also prevent the weak fiber from breaking. As stabilization progresses, tension loading is increased for the stronger and less-stretchable fibers.

[0062] For different lignin-based precursor fibers, the amount of tension loading is determined based on the T_g and strength of the precursors. Compared to stabilizing a precursor fiber with lower T_g , higher amounts of tension should be applied to the precursor fiber with higher T_g at an earlier stage of stabilization to ensure fibers are stretched. Applying insufficient tension to a high T_g precursor may not stretch fibers during stabilization, resulting in carbon fibers with poor qualities.

[0063] According to the present application, the lignin fiber can be stabilized at a tension of about 0.01 kPa to about 2000 kPa per fiber, 0.1 kPa to about 2000 kPa per fiber, about 0.5 kPa to about 2000 kPa per fiber, about 1.5 kPa to about 2000 kPa per fiber, about 2.0 kPa to about 2000 kPa per fiber, about 2.5 kPa to about 2000 kPa per fiber, about 3.0 kPa to about 2000 kPa per fiber, about 3.5 kPa to about 2000 kPa per fiber, about 4.0 kPa to about 2000 kPa per fiber, about 4.5 kPa to about 2000 kPa per fiber, about 5.0 kPa to about 2000 kPa per fiber, about 5.5 kPa to about 2000 kPa per fiber, about 6.0 kPa to about 2000 kPa per fiber, about 6.5 kPa to about 2000 kPa per fiber, about 7.0 kPa to about 2000 kPa per fiber, about 7.5 kPa to about 2000 kPa per fiber, about 8.0 kPa to about 2000 kPa per fiber, about 8.5 kPa to about 2000 kPa per fiber, about 9.0 kPa to about 2000 kPa per fiber, about 9.5 kPa to about 2000 kPa per fiber, about 10.0 kPa to about 2000 kPa per fiber, about 10.5 kPa to about 2000 kPa per fiber, about 11.0 kPa to about 2000 kPa per fiber, about 11.5 kPa to about 2000 kPa per fiber, about 12.0 kPa to about 2000 kPa per fiber, about 13.0 kPa to about 2000 kPa per fiber, about 14.0 kPa to about 2000 kPa per fiber, about 15.0 kPa to about 2000 kPa per fiber, about 16.0 kPa to about 2000 kPa per fiber, about 17.0 kPa to about 2000 kPa per fiber, about 18.0 kPa to about 2000 kPa per

fiber, about 19.0 kPa to about 2000 kPa per fiber, about 20.0 kPa to about 2000 kPa per fiber, about 1.5 kPa to about 1750 kPa per fiber, about 1.5 kPa to about 1500 kPa per fiber, about 1.5 kPa to about 1250 kPa per fiber, or about 1.5 kPa to about 1000 kPa per fiber.

[0064] In one embodiment, stabilization is carried out at the following temperatures and the following tensions:

[0065] at the temperature of about 25° C. to about 105° C., the tension is from about 0.1 kPa/fiber to about 10 kPa/fiber;

[0066] at the temperature of about 105° C. to about 135° C., the tension is from about 1.5 kPa/fiber to about 15 kPa/fiber;

[0067] at the temperature of about 135° C. to about 155° C., the tension is from about 1.5 kPa/fiber to about 100 kPa/fiber;

[0068] at the temperature of about 155° C. to about 200° C., the tension is from about 10 kPa/fiber to about 1000 kPa/fiber; and at the temperature of about 200° C. to about 300° C., the tension is from about 10 kPa/fiber to about 1200 kPa/fiber.

[0069] In one embodiment, the tension applied during the stabilization process stretches fibers to a length greater than its length prior to said stabilizing.

[0070] In another embodiment, the tension applied during the stabilizing process is increased in degree so that the lower amount tension is applied in the beginning of the stabilization process and the amount of the applied tension is gradually increased while the fiber is being stabilized.

[0071] According to the present application, the lignin fiber can be stabilized at different temperatures. The lignin fiber can be stabilized at a temperature of about 50° C. to about 500° C., about 75° C. to about 450° C., about 100° C. to about 300° C., about 105° C. to about 300° C., about 110° C. to about 300° C., about 110° C. to about 290° C., about 115° C. to about 280° C., about 120° C. to about 270° C., about 125° C. to about 260° C., or about 130° C. to about 250° C.

[0072] In some embodiments, during the stabilizing, the fiber is heated from a temperature of about 25° C. to a temperature of about 300° C. for over 2 to 30 hours. For example, the fiber is heated from a temperature of about 25° C. to a temperature of about 300° C. for over 2 hours, over 3 hours, over 4 hours, over 5 hours, over 6 hours, over 7 hours, over 8 hours, over 9 hours, over 10 hours, over 12 hours, over 15 hours, over 18 hours, or over 20 hours. The fiber can be heated from a temperature of about 25° C. to a temperature of about 300° C. for over 2 to 28 hours, over 4-25 hours, over 6-24 hours, over 8-20 hours, over 10-15 hours, over 2-26 hours, over 2-24 hours, over 2-22 hours, over 2-20 hours, over 2-18 hours, over 2-16 hours, over 2-14 hours, over 2-12 hours, over 4-26 hours, over 4-24 hours, over 4-22 hours, over 4-20 hours, over 4-18 hours, over 4-16 hours, over 4-14 hours, over 4-12 hours, over 6-26 hours, over 6-24 hours, over 6-22 hours, over 6-20 hours, over 6-18 hours, over 6-16 hours, over 6-14 hours, or over 6-12 hours.

[0073] In one embodiment, the lignin fiber is stabilized at varying temperatures, wherein the temperature is increased to stretch fiber and increase its T_g . In the initial stage of stabilization, the softened fiber is usually stretchable but very weak. As the stabilization temperature increases, the fiber hardens. As a result, the fiber becomes stronger than it

initially was, but it is more difficult to stretch. Thus, the stabilization temperature must be increased to stretch and harden fiber.

[0074] According to the present application, while the lignin fiber is being stabilized, the heating rate is adjusted. In some embodiments, when the heating rate is being adjusted based on the stabilization temperature being used, the reacting rate depends on the temperature that is being used during the stabilization process and the fiber condition. When fiber becomes harden, higher heating rates can be used to reduce stabilization time.

[0075] The total stabilization time for production of lignin-based carbon fiber can be shortened by subjecting the lignin-based carbon fiber to UV light treatment or UV irradiation before or during the stabilization process. Other techniques that can be used to enhance the stabilization process include thermal treatment (such as low-temperature pre-stabilization heat treatment), plasma assisted thermal treatment, plasma treatment, γ -rays irradiation, and microwave radiation.

[0076] In some embodiments, the lignin fiber is being stabilized until the fiber reached a certain diameter. For example, the lignin fiber is being stabilized until the fiber reached a diameter of about 0.1 μm to about 40 μm , about 0.1 μm to about 35 μm , about 0.1 μm to about 20 μm , about 1.0 μm to about 35 μm , about 2.0 μm to about 35 μm , about 3.0 μm to about 35 μm , about 4.0 μm to about 35 μm , about 5.0 μm to about 35 μm , about 5.0 μm to about 30 μm , about 2.5 μm to about 25 μm , about 2.0 μm to about 20 μm , about 2.5 μm to about 20 μm , about 3.0 μm to about 20 μm , about 3.5 μm to about 20 μm , about 4.0 μm to about 20 μm , about 4.5 μm to about 20 μm , about 5.0 μm to about 20 μm , about 5.5 μm to about 20 μm , or about 6.0 μm to about 20 μm . In some embodiment, the lignin fiber is being stabilized until the fiber reached a diameter of 10 μm or below. For example, the lignin fiber is being stabilized until the fiber reached a diameter below 9.9 μm , below 9.8 μm , below 9.7 μm , below 9.6 μm , below 9.5 μm , below 9.4 μm , below 9.3 μm , below 9.2 μm , below 9.1 μm , below 9.0 μm , below 8.9 μm , below 8.8 μm , below 8.7 μm , below 8.6 μm , below 8.5 μm , below 8.4 μm , below 8.3 μm , below 8.2 μm , below 8.1 μm , below 8.0 μm , below 7.9 μm , below 7.8 μm , below 7.7 μm , below 7.6 μm , below 7.5 μm , below 7.4 μm , below 7.3 μm , below 7.2 μm , below 7.1 μm , below 7.0 μm , below 6.9 μm , below 6.8 μm , below 6.7 μm , below 6.6 μm , below 6.5 μm , below 6.4 μm , below 6.3 μm , below 6.2 μm , below 6.1 μm , below 6.0 μm , below 5.9 μm , below 5.8 μm , below 5.7 μm , below 5.6 μm , below 5.5 μm , below 5.4 μm , below 5.3 μm , below 5.2 μm , below 5.1 μm , below 5.0 μm , below 4.9 μm , below 4.8 μm , below 4.7 μm , below 4.6 μm , below 4.5 μm , below 4.4 μm , below 4.3 μm , below 4.2 μm , below 4.1 μm , below 4.0 μm , below 3.9 μm , below 3.8 μm , below 3.7 μm , below 3.6 μm , below 3.5 μm , below 3.4 μm , below 3.3 μm , below 3.2 μm , below 3.1 μm , below 3.0 μm , below 2.9 μm , below 2.8 μm , below 2.7 μm , below 2.6 μm , below 2.5 μm , below 2.4 μm , below 2.3 μm , below 2.2 μm , below 2.1 μm , below 2.0 μm , below 1.9 μm , below 1.8 μm , below 1.7 μm , below 1.6 μm , below 1.5 μm , below 1.4 μm , below 1.3 μm , below 1.2 μm , below 1.1 μm , below 1.0 μm , below 0.9 μm , below 0.8 μm , below 0.7 μm , below 0.6 μm , below 0.5 μm , below 0.4 μm , or below 0.3 μm .

[0077] Adjustable parameters in the carbonization of the lignin-based carbon fiber include, but are not limited to, temperature, heating rate, and whether tension is applied.

[0078] According to the present application, the lignin fiber can be carbonized at different temperatures. The tension is applied during carbonization to make sure the fiber does not shrink back along the fiber axial direction. The stabilized fibers fabricated using the methods of the present application usually exhibit a high tendency for shrinking during carbonization. The fibers shrink more noticeably when carbonization temperature increases (e.g., to above 500° C.) or higher heating rates are employed during carbonization. Thus, either a constant tension is applied throughout the entire carbonization process, or tension is increased at higher carbonization temperatures to make sure the fiber doesn't shrink. Heating rate can be reduced at higher carbonization temperature region to prevent excessive fiber shrinkage and the breakage of the fibers under tension.

[0079] The lignin fiber can be carbonized at a temperature of about 100° C. to about 2000° C., about 200° C. to about 1750° C., about 300° C. to about 1500° C., about 400° C. to about 1250° C., about 450° C. to about 1200° C., about 500° C. to about 1200° C., about 550° C. to about 1200° C., about 600° C. to about 1200° C., about 500° C. to about 1100° C., about 500° C. to about 1000° C., about 500° C. to about 950° C., about 500° C. to about 900° C., about 500° C. to about 850° C., about 550° C. to about 800° C., about 600° C. to about 800° C., about 650° C. to about 750° C., or about 680° C. to about 720° C. In some embodiments, the lignin fiber can be carbonized at a temperature of about 650° C., about 660° C., about 670° C., about 680° C., about 690° C., about 700° C., about 710° C., about 720° C., or about 730° C.

[0080] The lignin fibers prepared according to the methods described in the present application can have an average diameter below 20 μm, below 19 μm, below 18 μm, below 17 μm, below 16 μm, below 15 μm, below 14 μm, below 13 μm, below 12 μm, below 11 μm, below 10 μm, below 9.9 μm, below 9.8 μm, below 9.7 μm, below 9.6 μm, below 9.5 μm, below 9.4 μm, below 9.3 μm, below 9.2 μm, below 9.1 μm, below 9.0 μm, below 8.9 μm, below 8.8 μm, below 8.7 μm, below 8.6 μm, below 8.5 μm, below 8.4 μm, below 8.3 μm, below 8.2 μm, below 8.1 μm, below 8.0 μm, below 7.9 μm, below 7.8 μm, below 7.7 μm, below 7.6 μm, below 7.5 μm, below 7.4 μm, below 7.3 μm, below 7.2 μm, below 7.1 μm, below 7.0 μm, below 6.9 μm, below 6.8 μm, below 6.7 μm, below 6.6 μm, below 6.5 μm, below 6.4 μm, below 6.3 μm, below 6.2 μm, below 6.1 μm, below 6.0 μm, below 5.9 μm, below 5.8 μm, below 5.7 μm, below 5.6 μm, below 5.5 μm, below 5.4 μm, below 5.3 μm, below 5.2 μm, below 5.1 μm, below 5.0 μm, below 4.9 μm, below 4.8 μm, below 4.7 μm, below 4.6 μm, below 4.5 μm, below 4.4 μm, below 4.3 μm, below 4.2 μm, below 4.1 μm, below 4.0 μm, below 3.9 μm, below 3.8 μm, below 3.7 μm, below 3.6 μm, or below 3.5 μm.

[0081] In some embodiments of the present application the lignin fibers prepared according to the methods described in the present application can have an average diameter about 0.1 μm to about 20 μm, about 1 μm to about 20 μm, about 2 μm to about 20 μm, about 1 μm to about 10 μm, about 1 μm to about 5 μm, 0.1 μm to about 5 μm, about 3.0 μm to about 20 μm, about 4.0 μm to about 20 μm, about 5.0 μm to about 20 μm, about 6.0 μm to about 20 μm, about 2 μm to about 15 μm, about 3.0 μm to about 15 μm, about 4.0 μm to about 15 μm, about 5.0 μm to about 15 μm, about 2 μm to

about 10 μm, about 3.0 μm to about 10 μm, about 4.0 μm to about 10 μm, about 5.0 μm to about 10 μm, or about 6.0 μm to about 10 μm.

[0082] The lignin fibers prepared according to the methods described in the present application can have an average tensile strength of about 0.5 GPa to about 5.0 GPa, about 1.0 GPa to about 5.0 GPa, about 2.0 GPa to about 5.0 GPa, about 2.5 GPa to about 5.0 GPa, about 3.0 GPa to about 5.0 GPa, about 0.5 GPa to about 4.0 GPa, about 1.0 GPa to about 4.0 GPa, about 2.0 GPa to about 4.0 GPa, about 2.5 GPa to about 4.0 GPa, about 3.0 GPa to about 4.0 GPa, about 0.5 GPa to about 3.0 GPa, about 1.0 GPa to about 3.0 GPa, about 2.0 GPa to about 3.0 GPa, or about 2.5 GPa to about 3.0 GPa.

[0083] The lignin fibers prepared according to the methods described in the present application can have an average tensile modulus of about 50 GPa to about 500 GPa, 100 GPa to about 500 GPa, about 100 GPa to about 400 GPa, about 100 GPa to about 300 GPa, about 150 GPa to about 300 GPa, about 150 GPa to about 250 GPa, about 200 GPa to about 250 GPa, about 200 GPa to about 300 GPa, about 200 GPa to about 400 GPa, or about 200 GPa to about 500 GPa.

[0084] The lignin fibers prepared according to the methods described in the present application can have inner pores. In some embodiments, inner pores of the lignin fibers have an average radius of about 0.1 nm to about 5 nm, about 0.2 nm to about 4.5 nm, about 0.3 nm to about 4 nm, about 0.4 nm to about 3.5 nm, about 0.5 nm to about 3 nm, about 0.6 nm to about 2.5 nm, about 0.7 nm to about 2.5 nm, about 0.8 nm to about 2.5 nm, about 0.9 nm to about 2.5 nm, about 1 nm to about 2.5 nm, about 0.5 nm to about 2.4 nm, about 0.6 nm to about 2.4 nm, about 0.7 nm to about 2.4 nm, about 0.8 nm to about 2.4 nm, about 0.9 nm to about 2.4 nm, about 1 nm to about 2.4 nm, about 0.5 nm to about 2.3 nm, about 0.6 nm to about 2.3 nm, about 0.7 nm to about 2.3 nm, about 0.8 nm to about 2.3 nm, about 0.9 nm to about 2.3 nm, about 1 nm to about 2.3 nm, about 0.5 nm to about 2.2 nm, about 0.6 nm to about 2.2 nm, about 0.7 nm to about 2.2 nm, about 0.8 nm to about 2.2 nm, about 0.9 nm to about 2.2 nm, about 1 nm to about 2.2 nm, about 0.5 nm to about 2.1 nm, about 0.6 nm to about 2.1 nm, about 0.7 nm to about 2.1 nm, about 0.8 nm to about 2.1 nm, about 0.9 nm to about 2.1 nm, about 1 nm to about 2.1 nm, about 0.5 nm to about 2.0 nm, about 0.6 nm to about 2.0 nm, about 0.7 nm to about 2.0 nm, about 0.8 nm to about 2.0 nm, about 0.9 nm to about 2.0 nm, or about 1 nm to about 2.0 nm.

[0085] Another aspect of the present application relates to the carbon fiber prepared according to any of the methods described above.

[0086] This aspect of the present application can be carried out with any of the embodiments disclosed herein.

[0087] Another aspect of the present application relates to a lignin-based carbon fiber comprising an elemental oxygen content of at least 1 wt %, an elemental carbon content of at least 65 wt %, an average diameter of about 0.1 μm to about 20 μm, an average tensile strength of from about 2.0 GPa to about 4.0 GPa, and an average tensile modulus of from about 200 GPa to about 400 GPa.

[0088] According to the present application, the lignin-based carbon fiber can have the elemental oxygen content from about 1 wt % to about 30 wt %, from about 2.5 wt % to about 30 wt %, from about 5 wt % to about 30 wt %, from about 7.5 wt % to about 30 wt %, from about 10 wt % to about 30 wt %, from about 10 wt % to about 29 wt %, from about 10 wt % to about 28 wt %, from about 10 wt % to

about 27 wt %, from about 10 wt % to about 26 wt %, from about 10 wt % to about 25 wt %, from about 10 wt % to about 24 wt %, from about 10 wt % to about 23 wt %, from about 10 wt % to about 22 wt %, from about 10 wt % to about 21 wt %, from about 10 wt % to about 20 wt %, from about 1 wt % to about 30 wt %, from about 12 wt % to about 30 wt %, from about 13 wt % to about 30 wt %, from about 14 wt % to about 30 wt %, from about 15 wt % to about 30 wt %, from about 16 wt % to about 30 wt %, from about 17 wt % to about 30 wt %, from about 18 wt % to about 30 wt %, from about 19 wt % to about 30 wt %, or from about 20 wt % to about 30 wt %.

[0089] According to the present application, the lignin-based carbon fiber can have the elemental carbon content from about 50 wt % to about 99 wt %, from about 55 wt % to about 95 wt %, from about 56 wt % to about 90 wt %, from about 57 wt % to about 90 wt %, from about 58 wt % to about 90 wt %, from about 59 wt % to about 90 wt %, from about 60 wt % to about 90 wt %, from about 61 wt % to about 90 wt %, from about 62 wt % to about 90 wt %, from about 63 wt % to about 90 wt %, from about 64 wt % to about 90 wt %, from about 65 wt % to about 90 wt %, from about 65 wt % to about 89 wt %, from about 65 wt % to about 88 wt %, from about 65 wt % to about 87 wt %, from about 65 wt % to about 86 wt %, from about 65 wt % to about 85 wt %, from about 66 wt % to about 90 wt %, from about 67 wt % to about 90 wt %, from about 68 wt % to about 90 wt %, from about 69 wt % to about 90 wt %, or from about 70 wt % to about 90 wt %.

[0090] Another aspect of the present application relates to a molded article for a machine part, electric and electronic part, or automotive part. The article comprising a matrix material and the carbon fiber of the present application dispersed in said matrix material.

[0091] Suitable matrix materials that can be used include polymers (resins), ceramics, or metals.

[0092] Resins that can be used include thermosetting resins such as a phenolic resin, a melamine resin, a urea resin, an unsaturated polyester resin, an alkyd resin, and thermosetting polyimide; thermoplastic resins such as polystyrene, an acrylonitrile/styrene resin, an acrylonitrile/butadiene/styrene resin, a methacrylic resin, polyethylene (PE), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), polyamide (PA or nylon), and polypropylene (PP); high-performance thermoplastic resins, such as polyetheretherketone (PEEK), polyetherketone (PEK), polyamide-imide (PAI), polyarylsulfone (PAS), polyetherimide (PEI), polyethersulfone (PES), polyphenylene sulfide (PPS), and liquid crystal polymer (LCP).

[0093] Other resins that can be used include engineering plastics such as polyacetal, ultrahigh molecular weight polyethylene and polycarbonate; and super engineering plastics such as polyphenylene sulfide, polyether ether ketone, a liquid crystal polymer, polytetrafluoroethylene, polyether imide, polyarylate and polyimide. In some embodiments, the matrix material is an epoxy resin (e.g., resins based on diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol F, creosol novolacs, or phenolic novolacs).

[0094] Matrix material may also include inorganic materials including metals such as aluminum, copper, titanium or silicon, or the oxides thereof.

[0095] In some embodiments, matrix material further includes one or more surfactants, and/or one or more dispersants, and/or one or more adhesives.

[0096] Suitable surfactants that can be used include amphoteric surfactants, anionic surfactants, cationic surfactants, and nonionic surfactants. Examples of the amphoteric surfactants that can be used include sulfobetaines, phosphobetaines, carboxybetaines, imidazolium betaines, and alkylamine oxides. Examples of the anionic surfactant that can be used include alkylbenzene sulfonate (e.g., C_{6-24} alkylbenzene sulfonate such as sodium laurylbenzenesulfonate, etc.), alkylnaphthalene sulfonate (e.g., di- C_{3-8} alkylnaphthalene sulfonate, such as sodium diisopropylnaphthalenesulfonate, etc.), alkyl sulfonate (e.g., C_{6-24} alkyl sulfonate such as sodium dodecanesulfonate, etc.), dialkylsulfosuccinic acid ester salt (e.g., di- C_{6-24} alkyl sulfosuccinate such as sodium di-2-ethylhexylsulfosuccinate, etc.), alkyl sulfate (e.g., sulfated grease, C_{6-24} alkyl sulfate such as a sodium salt of coconut oil-reduced alcohol), and alkyl phosphate (e.g., mono- to tri- C_{8-18} alkyl ester phosphate such as mono- to tri-lauryl ether phosphate, polyoxyethylene alkyl ether phosphate, etc.). Examples of the cationic surfactant include tetraalkylammonium salt (e.g., mono- or di- C_{8-24} alkyl-tri- or di-methylammonium salts such as lauryltrimethylammonium chloride or dioctadecyldimethylammonium chloride, etc.), trialkylbenzylammonium salt (e.g., C_{8-24} alkylbenzyltrimethylammonium salt such as cetylbenzyltrimethylammonium chloride (benzalkonium chloride salt, etc.), etc.), and alkylpyridinium salt (e.g., C_{8-24} alkylpyridinium salt such as cetylpyridinium bromide, etc.). Examples of the nonionic surfactant include polyoxyethylene alkyl ether (e.g., polyoxyethylene C_{6-24} alkyl ether such as polyoxyethylene octyl ether, polyoxyethylene lauryl ether or polyoxyethylene cetyl ether), polyoxyethylene alkylphenyl ether (e.g., polyoxyethylene C_{6-18} alkylphenyl ether such as polyoxyethylene octylphenyl ether or polyoxyethylene nonylphenyl ether, etc.), polyoxyethylene polyhydric alcohol fatty acid partial ester (e.g., polyoxyethylene glycerin C_{8-24} fatty acid ester such as polyoxyethylene glycerin stearic acid ester, polyoxyethylene sorbitan C_{8-24} fatty acid ester such as polyoxyethylene sorbitan stearic acid ester, polyoxyethylene sucrose C_{8-24} fatty acid ester, etc.), and polyglycerin fatty acid ester (e.g., polyglycerin C_{8-24} fatty acid ester such as polyglycerin monostearic acid ester).

[0097] In some embodiments, matrix material further includes one or more of the following: surface treatment agents (coupling agents such as a silane coupling agent, etc.), coloring agents (dyes and pigments, etc.), hue improving agents, dye fixing agents, glossing agents, metal corrosion preventing agents, stabilizers (an antioxidant, an ultraviolet absorber, etc.), dispersion stabilizing agents, thickeners or viscosity adjusting agents, thixotropic property-imparting agents, leveling agents, defoaming agents, disinfectants, fillers (milled fiber, chopped fiber, and glass microspheres), and flame or fire retardants.

[0098] In embodiments where the matrix material comprises a thermosetting resin, the matrix resin may further contain a curing agent or a curing accelerator. Specifically, the matrix material may comprise a resin (a thermosetting resin) and a curing agent or a curing accelerator for the resin. The curing agents may be used alone or in combination. The curing agent can also act as a curing accelerator.

[0099] The curing agent can be selected according to the species of the resin. For example, in a case where the resin

is an epoxy resin, the curing agent may include, for example, an amine-based curing agent, a phenolic resin-based curing agent (e.g., a phenol novolac resin and a cresol novolac resin), an acid anhydride-based curing agent (e.g., an aliphatic dicarboxylic anhydride (such as dodecenylsuccinic anhydride), an alicyclic dicarboxylic anhydride (such as tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, or hexahydrophthalic anhydride), and an aromatic dicarboxylic anhydride (such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, or benzophenonetetracarboxylic anhydride)), a polymercaptan-based curing agent, and a latent curing agent (such as boron trifluoride-amine complex, dicyandiamide, or a carbohydrazide).

[0100] Suitable amine-based curing agents that can be used include an aromatic amine-based curing agent, an aliphatic amine-based curing agent, an alicyclic amine-based curing agent, and an imidazole compound or a salt thereof (e.g., a formate, a phenol salt, a phenol novolac salt, and a carbonate). Examples of the aromatic amine-based curing agent that can be used include a polyaminoarene (e.g., a diaminoarene such as p-phenylenediamine or m-phenylenediamine), a polyamino-alkylarene (e.g., a diamino-alkylarene such as diethyltoluenediamine), a poly(aminoalkyl)arene (e.g., a di(aminoalkyl)arene such as xylylenediamine), a poly(aminoaryl)alkane (e.g., a di(aminoaryl)alkane such as diaminodiphenylmethane), a poly(amino-alkylaryl)alkane (e.g., a di(amino-alkylaryl)alkane such as 4,4'-methylenebis(2-ethyl-6-methylaniline)), a bis(aminoarylalkyl)arene (e.g., 1,3-bis[2-(4-aminophenyl)-2-propyl]benzene and 1,4-bis[2-(4-aminophenyl)-2-propyl]benzene), a di(aminoaryl) ether (e.g., diaminodiphenyl ether), a di(aminoaryloxy)arene (e.g., 1,3-bis(3-aminophenoxy)benzene), and a di(aminoaryl) sulfone (e.g., diaminodiphenylsulfone). Examples of the aliphatic amine-based curing agent that can be used include ethylenediamine, hexamethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and diethylaminopropylamine. Examples of the alicyclic amine-based curing agent that can be used include menthenediamine, isophoronediamine, bis(4-amino-3-methylcyclohexyl)methane, 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, and norbornanediamine. Examples of the imidazole compound that can be used include an alkylimidazole such as 2-methylimidazole, 2-phenylimidazole, 2-heptadecylimidazole, or 2-ethyl-4-methylimidazole; and an arylimidazole such as 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, or 1-benzyl-2-phenylimidazole.

[0101] In some embodiments, matrix material further includes one or more hardeners. Suitable hardeners that can be used include aliphatic amines, cycloaliphatic amines, polyamides, aromatic amines, anhydrides, phenols, thiols, and latent hardeners (e.g., Lewis acids).

[0102] In one embodiment, the molded article is an automotive part. According to the present application, the automotive part that can be prepared using the carbon fiber of the present application is a hood, a pillar, a panel, a structural panel, a door panel, a door component, an interior floor, a floor pan, a roof, an exterior surface, an underbody shield, a wheel component, a storage area, a glove box, a console box, a trunk, a trunk floor, a truck bed, a lamp pocket, a shock tower cap, a control arm, a suspension component, a crush

can, a bumper, a structural rail, a structural frame, a cross car beam, an undercarriage component, a drive train component, or combinations thereof.

[0103] The above disclosure is general. A more specific description is provided below in the following examples. The examples are described solely for the purpose of illustration and are not intended to limit the scope of the present application. Changes in form and substitution of equivalents are contemplated as circumstances suggest or render expedient. Although specific terms have been employed herein, such terms are intended in a descriptive sense and not for purposes of limitation.

EXAMPLES

[0104] The following Examples are presented to illustrate various aspects of the present application, but are not intended to limit the scope of the claimed application.

Example 1—Lignin Preparation

[0105] As-received softwood organosolv (OL) and softwood Indulin kraft lignin (KL) produced from industrial processes were washed in 90° C. deionized water for 4 hours using a magnetic stirring bar to remove water-soluble impurities. The washed lignin was filtered and vacuum-dried overnight at 40° C. and kept in a sealed container before use.

Example 2—Carbon Fiber (CF) Production Method

[0106] Melt spinning of lignin precursors was performed using a bench-top twin-screw micro compounder (DACA Instruments, Santa Barbara, CA) with a nozzle size of 2 mm, and fibers were collected on a roller (DSM, Geleen, the Netherlands) at 100 m/min. When OL alone was used, the lignin powder was directly injected into the extruder for fiber spinning. For preparing blended lignin precursors, OL and KL were first mixed in the extruder to make pellets. The mixing temperature was 185° C. for the 90/10 (w/w) OL/KL blend and 195° C. for the 80/20 (w/w) blend. The rotation speed was 150 rpm for both blends. The pellets were then re-injected into the extruder for fiber spinning. The extruder temperature and rotation speed were 155° C. and 100 rpm for OL 195° C. and 100 rpm for 90/10 OL/KL and 205° C. and 120 rpm for 80/20 OL/KL respectively.

[0107] Stabilization was performed using a Isotemp programmable forced-Draft furnace (Fisher Scientific; 12×6 inch dimension) using air. Before stabilization, the as-spun fiber (AF) bundle (FIG. 1A) was cut into a length of 2 cm. Each end of the fiber bundle was held between two graphite strips using epoxy glue (FIG. 1B). The fibers and the graphite strip assembly were vertically hung inside the furnace. Tension was applied by attaching weights to the bottom of the fiber assembly via a hook. The amount of tension stress applied to a single fiber was calculated by dividing the total gravity weight applied on the fibers (i.e., the sum of the mass of the fibers, the graphene strips, epoxy, hook, and the metal weights) by the cross-sectional area of the fiber bundles and the number of the fibers. While the weights were adjusted multiple times during the stabilization, the cross-sectional areas of the fiber bundles were measured only when the adjustments were made to calculate the tensile stress of the fibers at the times of the adjustments.

[0108] Carbonization of stabilized fiber (SF) was conducted in a tubular furnace (Lindberg Blue M, Thermo Scientific) purged by nitrogen gas. Before carbonization, the

SF bundle was placed onto a graphite sheet, and the ends of the fiber were fixed using a high-temperature glue (Cerama-bond 503) and graphite strips. The fibers were carbonized from room temperature to 500° C. at 7° C./min, 5 min at 500° C., from 500° C. to final temperatures at 2° C./min, and then kept for an hour. The final temperature was between 500 to 1000° C. for OL-based fibers, 700 to 800° C. for 90/10 OL/KL-based fibers, and 700° C. for 80/20 OL/KL lignin.

[0109] For comparison studies, tension-free fibers derived from 100% OL were placed on an alumina boat in the furnace and oven for stabilization and carbonization.

Example 3—Characterization Methods

[0110] Gel Permeation Chromatography (GPC) analysis was conducted to determine the molecular weight distribution of lignin. A Dionex Ultimate 3000 series high-performance liquid chromatograph (HPLC) was equipped with a Shodex Refractive Index (RI) and Diode Array Detectors (DAD). Two Agilent PLgel 3 μ m 100A0 300 $\times$ 7.5 mm (p/n PL1110-6320) columns were connected in series and maintained at 25° C. An ultraviolet wavelength of 254 nm was used to detect the peaks. A GPC column was calibrated with six monodisperse polystyrene standards ranging from 162 to 45120 g/mol. Tetrahydrofuran (THF), with a flow rate of 1 mL/min, was used as solvent and eluent in the column. The lignin samples were acetylated before the GPC analysis to increase their solubility using a previous method (Zhou et al., “Lignin Valorization Through Thermochemical Conversion: Comparison of Hardwood, Softwood and Herbaceous Lignin,” *ACS Sustain. Chem. Eng.* 4(12):6608-6617 (2016), which is hereby incorporated by reference in its entirety). Briefly, 100 mg of lignin was placed in a glass vial, and 3 mL of pyridine and 3 mL of acetic anhydride were added. The mixture was heated in an oil bath at 80° C. for three hours under continuous agitation. After the reaction, the solution was added to 500 mL of deionized water to precipitate the acetylated lignin. Precipitated lignin was filtered and washed with deionized water three times to remove the unreacted pyridine and acetic anhydride.

[0111] Proximate analysis of lignin was performed using a thermal gravimetric analyzer (TGA/DSC 1 STARe system, Mettler Toledo). About 20 mg of vacuum-dried lignin was pyrolyzed at 10° C./min to 900° C. using nitrogen with a flow rate of 100 mL/min. After staying at 900° C. for 30 min, the air was introduced for combustion.

[0112] The glass transition temperature of lignin was determined using a DSC (Q2000, TA instruments). The sample was first rapidly heated to 200° C. and then cooled to 25° C. to eliminate thermal history. The sample was reheated to 200° C. at a heating rate of 10° C./min to determine T_g .

[0113] Tensile properties of fibers were measured using a Discovery hybrid rheometer (DHR-2, TA Instruments) with dynamic mechanical analysis clamps by following an ASTM standard (ASTM C1557-03) based on single filament testing protocol. Data was acquired with a 0.001s interval during the test. The fiber diameter was determined using a calibrated Leica LED inverted laboratory microscope with 20 $\times$ magnification lens with a resolution of 1. Each fiber diameter measurement was an average of 5 locations along the fiber axial direction. The results of an average of 20 fibers were reported with a 95% confidence interval.

[0114] Scanning Electron Microscopy (SEM) analysis of carbon fiber (CF) was performed using FEI Inspect F50 Scanning Electron Microscope.

[0115] Transmission Electron Microscopy (TEM) analysis of CF was performed using a JEOL 2100 scanning TEM (Japan Electron Optics Laboratories) with a Gatan OneView 4K camera (Gatan, Inc) and an operating voltage of 200 kV. ImageJ was used to determine crystallite size.

[0116] For preparing samples for Heteronuclear-single-quantum-coherence nuclear magnetic resonance (HSQC-NMR) analysis, 100 mg of fibers were dissolved in 1 mL of 4:1 (v/v) mixture of dimethyl sulfoxide (DMSO)-d₆ and pyridine-d₅ and sonicated for 2 hours. HSQC spectroscopies were obtained on a Bruker Biospin Advance 600 MHz spectrometer incorporated with a 5 mm cryogenically cooled z-gradient probe using the Bruker pulse sequence “hsqcetg-psisp.2”. The data processing was carried out using MestReNova v12.0.1 software.

[0117] Fourier Transform Infrared (FTIR) analysis was conducted using a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) with a Smart iTR accessory. The wave numbers of the FTIR analysis ranged from 750 to 4000 cm^{-1} . Each sample was scanned 32 times at a resolution of 4 cm^{-1} and an interval 1 cm^{-1} .

[0118] Fast pyrolysis was performed using a Frontier micropyrolyzer system with an auto-shot sampler (Rx-3050 TR, Frontier Laboratories, Japan) and a single-stage furnace oven. Before pyrolysis, ball-milled fibers were kept in a sealed container. During pyrolysis, approximately 0.5 mg of the sample in a deactivated stainless cup was dropped into a furnace preheated to 550° C. Pyrolysis vapor products were directly swept into an online GC/MS. Helium was used as both the pyrolysis and carrier gas. An Agilent 7890B GC equipped with Agilent 5977A mass-selective detector (MSD), flame ionization detector (FID), and thermal conductivity analyzer (TCD) was used. The capillary column used in the GC was a ZB-1701 (60 m $\times$ 250 mm $\times$ 0.25 mm). The injection temperature at the GC was 250° C. The oven temperature was kept at 40° C. for 3 min and then ramped to 280° C. at 3° C./min. Finally, the oven was held at 280° C. for another 4 minutes. The GC inlet temperature was maintained at 280° C. The helium gas flow rate was 1 mL/min, and the split ratio at the GC inlet was 20 to 1.

[0119] The elemental composition of fibers was determined using an elemental analyzer (Vario Micro Cube, Elementar, Germany). Carbon, hydrogen, nitrogen, and sulfur contents were measured, and oxygen content was determined by mass difference. The ash content of lignin was subtracted before calculating the elemental compositions.

[0120] Raman analysis of fibers was conducted using a confocal Raman system (Voyage, B&W Tek, Inc., Olympus BX51). A 532 nm Raman laser of 16 mW was focused on the fiber with a 503 lens. The measurement was conducted in two different views of the fibers. A 20 s integration time was used to obtain the spectrum, and Origin software was used to analyze the acquired Raman spectra with Gaussian curve fitting.

[0121] The crystallographic analysis of CF was conducted using an XRD (Siemens D500 diffractometer) using Copper K α radiation ($\lambda=1.5432$ Å) with an accelerating voltage of 45 kV and current of 30 mA within the range of 2θ from 10° to 70° and a dwell time of 2s. The fiber bundles were used, and equatorial scans were performed perpendicularly and parallel to the fiber axis.

[0122] A Xenocs Xueess 2.0 system with Cu (1.5406 Å) radiation was used to collect XPS data of CF. In the XPS spectra, C1 spectra were deconvoluted into four Gaussian peaks: —C—C—, —C—H— at 284.8 eV, —C—O— at 286.3 eV, C=O at 288.0 eV, and —O—C=O at 289.1 eV.

[0123] A Xenocs Xueess 2.0 system with Cu (1.5406 Å) radiation was used to collect Small-angle X-ray Scattering (SAXS) data.

Example 4—Data Analysis

Analysis of CF Raman Results

[0124] The broad D and G bands in the Raman spectra shown in FIGS. 2A and 2B were deconvoluted into five bands using the Gaussian curve fitting for calculating the I_D/I_G ratio of CFs. D_1 peak at 1360 cm^{-1} and the D_2 peak at 1620 cm^{-1} are disordered carbon in hexagonal carbon layers or at the edges of crystallites. D_3 (1500 cm^{-1}) between D_1 and G (1580 cm^{-1}) and D_4 (1200 cm^{-1}) at the left shoulder of the broad D band is derived from sp^2 -bonded amorphous carbon. The peak area sum of D_1 and D_2 divided by the peak area of G was used to calculate the I_D/I_G ratio, representing the disordered sp^2 attached to graphite structures. A lower I_D/I_G ratio represents a higher ordering and reduced structural defect.

Analysis of XRD Results

[0125] Before calculating crystalline parameters, Gaussian curve fitting was performed on the broad first band to deconvolute the 002 and γ bands. The Bragg and Scherrer formula was used to calculate crystalline parameters, including interlayer spacing (d_{002}), stacking height (L_c), and lateral length (L_a), as shown below:

$$d_{002} = \lambda / 2 \sin \theta \quad (\text{Eq. 1})$$

$$L = K \lambda \beta \cos \theta \quad (\text{Eq. 2})$$

where θ is the Bragg angle of the corresponding peak; λ is the wavelength of the X-ray; constant K is 0.89 for the (002) band and 1.84 for (β); R is the full width at half maximum intensity (FWHM) of the (002) peak and (100) peak; θ is the scattering angle of the corresponding peak. The (002) band measured from the parallel scan was used to calculate L_c , and the (100) band measured from the perpendicular scan was used to calculate L_a .

Analysis of SXAS Results

[0126] The SAXS results (FIG. 3) were used to calculate average pore diameters of CF based on a modified form of the Kalliat model (Kalliat et al., “Small-Angle X-Ray Investigation of the Porosity in Coals,” in Blaustein et al. eds., *New Approaches in Coal Chemistry*, Vol. 169, American Chemical Society, pp. 3-22 (1981), which is hereby incorporated by reference in its entirety) for SXAS measurement by McDonald et al., “A Study of Small Angle X-Ray Scattering from Impregnated Activated Carbons,” *Carbon N. Y.* 68:452-461 (2014), which is hereby incorporated by reference in its entirety, shown below:

$$I(q) = \rho^2 I_{OK} \left[\frac{A}{q^n} + \frac{C_{mi}}{(1 + b^2 q^2)^2} \right] + bkg \quad (\text{Eq. 3})$$

$$\text{the } R = \sqrt{10b} \quad (\text{Eq. 4})$$

where $I(q)$ is the scattering intensity of the fibers; ρ is the electronic density of graphite; I_{OK} is a parameter associated with the sample mass, the cross-section area of the sample, and the area of the X-ray beam penetrating the sample; q is the wave vector; A is proportional to the surface area of pores; C_{mi} is proportional to the volume of pores, and b is the Debye autocorrelation length of the pores; R is the radius of the pores; and bkg is the background. n was set up as 3 (for scattering from rough fractal surfaces). While CFs have a distribution of pore sizes, it has been proven that a single characteristic pore size is enough for a reasonable fit to the data instead of a distribution of pore sizes (Kalliat et al., “Small-Angle X-Ray Investigation of the Porosity in Coals,” in Blaustein et al. eds., *New Approaches in Coal Chemistry*, Vol. 169, American Chemical Society, pp. 3-22 (1981), which is hereby incorporated by reference in its entirety).

Example 5—Techno-Economic Analysis (TEA) Modeling

[0127] The Techno-Economic Analysis Modeling was performed based on the study by Ellringmann et al., “Carbon Fiber Production Costing: A Modular Approach,” *Text. Res. J.* 86(2):178-190 (2016), which is hereby incorporated by reference in its entirety, and validated based on the U.S. DOE 2021 Carbon Fiber report (Adams et al., “Consortium for Production of Affordable Carbon Fibers in the United States (Final Report),” United States (2021), which is hereby incorporated by reference in its entirety). The base case facility produces 10,000 metric tonnes of CF per year from lignin using a solvent-free melt-spinning process.

[0128] Annualized capital costs for the facility were estimated using the formula:

$$\text{Capital} = DF * \text{Investment} * \text{area} \quad (\text{Eq. 5})$$

where DF is the capital discount factor given a project lifetime n (20 years) with an interest rate i (10%), and it is defined as:

$$DF = \frac{1}{(1 + i)^n} \quad (\text{Eq. 6})$$

The Investment factor is the cost per m^2 of the facility, which is $\$1386/\text{m}^2$ based on Ellringmann et al., “Carbon Fiber Production Costing: A Modular Approach,” *Text. Res. J.* 86(2):178-190 (2016), which is hereby incorporated by reference in its entirety. The area was calculated from the number of manufacturing lines required. A typical manufacturing line can process 1,500 metric tonnes of CF per year, and each manufacturing line occupies 8650 m^2 . The manufacturing line cost was scaled up from 1.5 to 10 hours of stabilization time using a 0.7 economies-of-scale factor. Other capital-related costs include maintenance, insurance, and property tax, calculated as 3%, 0.5%, and 1% of the annual capital cost. CF capital cost can vary significantly due to several development factors, such as equipment type, stabilization time, and facility capacity. A DOE facility survey found that capital costs for commercial facilities

varied between \$110,000 and \$400,000 when scaled to a common capacity of 10,000 metric tonnes of carbon fiber per year.

[0129] Operating costs included material and utility costs. The main material is lignin. Lignin is available from different commercial sources, including pulp and paper mills and lignocellulosic biorefineries. Many factors, including the quality and condition of the lignin, and alternative markets, can influence the price of lignin. According to the DOE national laboratories, lignin prices range between \$44 and \$176 per metric tonne. For this solvent-free process, the cost of chemicals was assumed to be negligible. Utility costs were estimated at 28.69 kWh/kg of CF with an electricity price of 0.0692. The electricity consumption was adjusted based on the CF conversion efficiency with a baseline of 0.476 corresponding to PAN to CF.

Example 6—Results and Discussion of Examples 1-5

CF Production Using a Thermo-Mechanically Controlled Fabrication Method

[0130] The mass recovery after water-washing was 95% for OL and 98% for KL. The characterizations of the purified lignins are shown in Table 1. OL was melt-spinnable, whereas KL did not soften upon heating. Thus, melt-spinnable precursors were prepared using either OL alone or blending OL and KL. The three precursors were 100% OL, 90/10 (w/w) OL/KL blend, and 80/20 (w/w) OL/KL blend. Their respective T_g was 74° C., 99° C., and 106° C.

TABLE 1

Lignin Characterizations After Water Purification				
	Raw OL	Water washed OL	Raw KL	Water washed KL
M_w (g/mol)	2791	3091	4580	5505
Dispersity	4.39	3.8	4.82	4.53
T_g (° C.)	95	74	198	156
T_d (° C.)	178	196	269	280
Moisture content (%)	1.2	1.22	2.34	1.25
Ash content (%)	1.4	0.07	2.59	0.55
Fixed carbon (%)	37.4	38.7	38.80	39.2

T_d : temperature corresponding to 5% mass loss

[0131] AF bundles were stabilized in the air by controlling heating rates and tension applied to the fibers. The heating and tension profiles were tuned for individual precursors based on the respective fibers' rheological behavior and mechanical strength during stabilization (FIGS. 4A-4C). For all AFs, their viscosity decreased rapidly once the softening points of lignin were reached. Therefore, lower heating rates were used near their softening temperatures to prevent fiber fusing. On the other hand, applying tension to the softened fiber can significantly reduce fiber diameters. However, AFs at the initial stage of the stabilization were very weak and easily broken if the tension force was over the limit. The fibers became less fusible and mechanically stronger as the stabilization progressed. Thus, heating rates and tension loading were adjusted in the course of the stabilization. Higher heating rates were used to reduce the stabilization time without causing fiber fusing. The weight loading was also periodically increased to ensure the stabilizing fibers

were always exposed (nearly under) maximum tension force. For different lignin precursors, overall higher heating rates were applied to a higher T_g precursor because the fiber was less fusible than a lower T_g precursor. On the other hand, a higher T_g precursor-based fiber also hardened faster than a lower T_g precursor-based fiber at the same temperatures. Thus, weight loading was increased sooner from lower stabilization temperatures to ensure the stabilizing fibers were continually under strong tension force. Due to how the tension was applied (the mechanical loading could not be adjusted continuously and fiber diameter monitoring was also unavailable due to the instrument limitation), the fiber diameters were only measured when the weight loading was adjusted. Thus, FIGS. 4A-4C only show the tension stresses of the fibers when the weight adjustment occurred. However, the fiber stresses are expected to increase between the intervals of weight adjustments due to decreasing fiber diameters during stabilization. Compared to the methods used in previous studies where tension was either not applied or softened fibers were stretched using small amounts of tension, the tension profile and heating profile were carefully integrated to ensure that lignin undergoing thermal stabilization was always exposed to near maximum tension forces that the changing lignin structures can bear. At the end of stabilization, not only the fiber length stretched by around 10 times (FIGS. 1C-1D), but it could also tolerate considerably high-tension loading, strikingly different from the weak initial fibers.

[0132] During the subsequent carbonization process, the SF produced using the present method exhibited a strong tendency to shrink in the axial direction when the carbonization temperature exceeds ~500° C. Such a phenomenon was not seen with previously produced lignin-based CFs. The fiber shrinkage was prevented mechanically by placing the SFs on a graphite sheet base and fixing the two ends of the fiber bundles using a high-temperature adhesive. This way, external tension force created by the adhesive and graphite sheet can overcome fiber shrinkage. Previously, SFs were either carbonized using a single heating rate or stepwise heating with increasing heating rates at higher temperature regions (Qu et al., "Towards Producing High-Quality Lignin-Based Carbon Fibers: A Review of Crucial Factors Affecting Lignin Properties and Conversion Techniques," *Int. J. Biol. Macromol.* 189:768-784 (2021), which is hereby incorporated by reference in its entirety). The present method is different from the previous method as a stepwise heating with a lower heating rate at higher temperatures was used. This is because higher heating rates can lead to greater fiber shrinkage. It was found that the OL-based SF carbonized using a single heating rate of 7° C./min shrunk so severely that the shrinkage even caused the graphene sheet holder to bend along the fiber direction and break fibers (FIGS. 5A-5B). The excessive shrinkage of the fibers was avoided by using a lower carbonization rate at higher temperatures.

[0133] The yields of CFs were 48-50% for lignin and lignin blends. The microscopic images of selected CFs are shown in FIGS. 6A-6D. The tensile properties of the present CFs and previous CFs are shown in Table 2. The average tensile strength and modulus of the 10000 OL-based CFs produced at a carbonization temperature of 600° C. were 1.06 GPa and 84 GPa and increased significantly to 2.45 GPa and 236 GPa for the CFs produced at 700° C. On the other hand, the average fiber diameter decreased from 6.1

μm to 3.3 μm in the corresponding fibers. Interestingly, further increasing carbonization temperatures increased fiber diameters and caused the tensile properties to decrease. The CFs produced at 800, 900, and 1000° C. had average fiber diameters of 4.3, 4.4, and 5.9 μm , and had tensile strength and modulus of 2.12 GPa and 189 GPa, 1.81 GPa and 178 GPa, and 1.27 GPa and 130 GPa, respectively. The increased CF diameters were due to the increased fiber shrinkage at higher carbonization temperatures. The same temperature dependencies of the tensile properties and fiber diameters were also observed with OL/KL-based CFs. The

tensile properties of 90/10% OL-based CFs were 2.11 GPa and 215 GPa for the carbonization temperature of 700° C., 2.08 GPa and 194.1 GPa for 750° C., and 1.94 GPa and 175.8 GPa for 800° C. For 80/20 OL/KL, the CF produced at 700° C. had the tensile properties of 2.2 GPa and 225 GPa (higher temperatures were not tested). Representative strain-stress curves of the CFs produced at 700° C. are shown in FIG. 7. Compared to previous results, CFs with superior tensile properties were obtained using unprecedentedly low carbonization temperature (Table 2).

TABLE 2

Lignin-Based Carbon Fibers Produced in This Disclosure and Previous Literature Studies						
Precursors	Fiber spinning method	Carbonization temperature (° C.)	Tensile strength (MPa)	Tensile modulus (GPa)	Fiber diameter (μm)	Ref.
Lignin or lignin blends						
Softwood organosolv lignin	melt	600	1060	84	6.1	this work
	melt	700	2456	236	3.4	this work
	melt	800	2122	189	4.3	this work
	melt	900	1809	178	4.4	this work
	melt	1000	1272	130	5.9	this work
Softwood organosolv lignin and kraft lignin (90/10)	melt	700	2110	215	3.3	this work
	melt	750	2082	198	3.6	this work
	melt	800	1941	176	3.8	this work
Softwood organosolv lignin and kraft lignin (80/20)	melt	700	2200	225	4.1	this work
Hardwood kraft lignin	melt	1000	605	61	46 $\pm$ 8.0	^a
Softwood kraft lignin and hardwood kraft lignin (90/10)	melt	1000	300	30	20-90	^b
Alcell organosolv lignin	melt	1000	720	45.9	8.5	^c
Softwood kraft lignin	melt	1200	465	32	39-65	^d
Switchgrass organosolv lignin	melt	1000	587	35	16.2 $\pm$ 6.0	^e
Yellow poplar organosolv lignin and switchgrass organosolv lignin (85/15)	melt	1000	747	42	15.7	^f
Solvent fractionated ultra-high molecular weight softwood kraft lignin	dry	1000	1390	98	7	^g
Chemically modified lignin						
Steam exploded hardwood lignin after hydrogenation	melt	1000	660	45	7.6 $\pm$ 2.7	^h
Phenolyzed steam exploded lignin	melt	1000	394	36	—	ⁱ
Acetylated softwood kraft lignin	dry	1000	1040	52	6-8	^j
Pyrolysis oil of hardwood lignin	melt	1000	855	85	29-50	^k
Peracylated softwood kraft lignin	melt	1000	750	34	17	^l
Acetylated corn stover organosolv lignin	melt	1000	454	62	39.1 $\pm$ 5.4	^m
Oleic acid functionalized lignin	melt	1000	640	71	24.8 $\pm$ 4.3	ⁿ

TABLE 2-continued

Lignin-Based Carbon Fibers Produced in This Disclosure and Previous Literature Studies						
Precursors	Fiber spinning method	Carbonization temperature (° C.)	Tensile strength (MPa)	Tensile modulus (GPa)	Fiber diameter (μm)	Ref.
Acrylate thermoplastic polymer synthesized using pyrolysis oil of lignin	melt	1000	1700	182	5.1	^o
Lignin and additives						
Hardwood kraft lignin and poly (ethylene oxide) (97/3)	melt	1000	458	59	33 ± 2	^p
Hardwood kraft lignin and polyethylene terephthalate (75/25)	melt	1000	703	94	34 ± 5	^a
Hardwood kraft lignin and syndiotactic polypropene (87.5/12.5)	melt	1000	437	54	44 ± 5	^a
Pyrolysis oil of lignin and 1% organoclay	melt	1000	438	32	47 ± 1	^q
Hardwood organosolv lignin and thermoplastic polyurethane (50/50)	melt	1400	1100	80	25 ± 3	^r
Hydroxyl-modified hardwood kraft lignin and thermoplastic polyurethane (50/50)	melt	1400	800	66	30 ± 1	^r
Pyrolysis oil of hardwood lignin and polyethylene terephthalate (95/5)	melt	1000	925	98	12.6 ± 2.1	^s
Kraft lignin, polyvinyl alcohol, and graphene oxide (66/29/5)	wet	1000	763	52	—	^t
Softwood kraft lignin and cellulose (70/30)	wet	1000	1070	76	7.6 ± 0.7	^u
Lignin and PAN						
Softwood kraft lignin and PAN (35/65)	wet	1200	1680	201	16.8	^v
Annual plant soda lignin and PAN (30/70)	gel (−50° C.)	1100	1720	250	11.0 ± 1.1	^w
Annual plant soda lignin, PAN, carbon nanotube (30/70/3)	gel (−50° C.)	1100	1400	200	8.8 ± 0.3	^w
Lignosulfonate and acrylonitrile co-polymer (10/90)	wet	1400	649	—	19.2	^x

TABLE 2-continued

Lignin-Based Carbon Fibers Produced in This Disclosure and Previous Literature Studies						
Precursors	Fiber spinning method	Carbonization temperature (° C.)	Tensile strength (MPa)	Tensile modulus (GPa)	Fiber diameter (μm)	Ref.
Softwood kraft lignin and PAN (50/50)	wet	1200	1200	105.7	7.0 ± 0.3 ^y	

^a Kubo et al., “Lignin-Based Carbon Fibers: Effect of Synthetic Polymer Blending on Fiber Properties,” *J. Polym. Environ.* 13(2): 97-105 (2005)

^b Nordström et al., “A New Softening Agent for Melt Spinning of Softwood Kraft Lignin,” *J. Appl. Polym. Sci.* 129(3): 1274-1279 (2013)

^c Baker et al., “Thermal Engineering of Lignin for Low-Cost Production of Carbon Fiber,” The Fiber Society 2009 Fall Meeting and Technical Conference (2009)

^d Salmén et al., “Extrusion of Softwood Kraft Lignins as Precursors for Carbon Fibres,” *BioResources* 10(4): 7544-7554 (2015)

^e Meek et al., “Synthesis and Characterization of Lignin Carbon Fiber and Composites,” *Compos. Sci. Technol.* 137: 60-68 (2016)

^f Hosseinaei et al., “Improving Processing and Performance of Pure Lignin Carbon Fibers through Hardwood and Herbaceous Lignin Blends,” *Int. J. Mol. Sci.* 18(7): 1410 (2017)

^g Jin et al., “Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance,” *ACS Sustain. Chem. Eng.* 6(11): 14135-14142 (2018)

^h Sudo et al., “A New Carbon Fiber from Lignin,” *J. Appl. Polym. Sci.* 44(1): 127-134 (1992)

ⁱ Sudo et al., “A New Modification Method of Exploded Lignin for the Preparation of a Carbon Fiber Precursor,” *J. Appl. Polym. Sci.* 48(8): 1485-1491 (1993)

^j Zhang et al., “Carbon Fibers from Dry-Spinning of Acetylated Softwood Kraft Lignin,” *Carbon N. Y.* 69: 626-629 (2014)

^k Qu et al., “Repolymerization of Pyrolytic Lignin for Producing Carbon Fiber with Improved Properties,” *Biomass and Bioenergy* 95: 19-26 (2016)

^l Steudle et al., “Carbon Fibers Prepared from Melt Spun Peracylated Softwood Lignin: an Integrated Approach,” *Macromol. Mater. Eng.* 302(4): 1-11 (2017)

^m Qu et al., “Potential of Producing Carbon Fiber from Biorefinery Corn Stover Lignin with High Ash Content,” *J. Appl. Polym. Sci.* 135(4): 1-11 (2018)

ⁿ Kang et al., “Carbon Fibers Derived from Oleic Acid-Functionalized Lignin via Thermostabilization Accelerated by UV Irradiation,” *ACS Sustain. Chem. Eng.* 9(14): 5204-5216 (2021)

^o Luo et al., “Enabling High-Quality Carbon Fiber Through Transforming Lignin into an Orientable and Melt-Spinnable Polymer,” *J. Clean. Prod.* 307: 127252 (2021)

^p Kadla et al., “Lignin-Based Carbon Fibers for Composite Fiber Applications,” *Carbon N. Y.* 40(15): 2913-2920 (2002)

^q Qin et.al., “Effect of Organoclay Reinforcement on Lignin-Based Carbon Fibers,” *Ind. Eng. Chem. Res.* 50(22): 12548-12555 (2011)

^r Culebras et al., “Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors,” *ACS Sustain. Chem. Eng.* 6(7): 8816-8825 (2018)

^s Qu et al., “Thermal Treatment of Pyrolytic Lignin and Polyethylene Terephthalate Toward Carbon Fiber Production,” *J. Appl. Polym. Sci.* 137(26): 1-10 (2020)

^t Torres-Canas et al., “Improved Structure and Highly Conductive Lignin-Carbon Fibers Through Graphene Oxide Liquid Crystal,” *Carbon N. Y.* 163: 120-127 (2020)

^u Bengtsson et al., “Carbon Fibers from Lignin-Cellulose Precursors: Effect of Carbonization Conditions,” *ACS Sustain. Chem. Eng.* 8(17): 6826-6833 (2020)

^v U.S. Patent Application Publication No. 2012/0003471 to Bissett et al.

^w Liu et al., “Processing, Structure, and Properties of Lignin- and CNT-Incorporated Polyacrylonitrile-Based Carbon Fibers,” *ACS Sustain. Chem. Eng.* 3(9): 1943-1954 (2015)

^x Ouyang et al., “Fabrication of Partially Biobased Carbon Fibers from Novel Lignosulfonate-Acrylonitrile Copolymers,” *J. Mater. Sci.* 52(12): 7439-7451 (2017)

^y Jin et al., “Carbon Fibers Derived from Wet-Spinning of Equi-Component Lignin/Polyacrylonitrile Blends,” *J. Appl. Polym. Sci.* 135(8): 1-9 (2018)

references ^{a-y} are hereby incorporated by reference in their entirety

Comparison of CFs Produced Using Different Processing Conditions

[0134] The present CFs were produced from sole lignin without chemical treatments or additives. Instead of modifying precursors, the spun fibers undergoing stabilization and carbonization were thermo-mechanically controlled. To show that the high quality of the CFs obtained is not related to the lignin sources but due to the fiber fabrication method, OL-based CFs were also fabricated using the same heating profiles described above for stabilization and carbonization but without tension control. For convenience, acronyms were used to indicate the fibers and their processing conditions (Table 3), with “T” indicating controlled tension, “N” indicating no tension, and “P” indicating controlled tension during stabilization but no tension during carbonization (i.e., partial tension). The numerical values in the acronyms represent the carbonization temperatures for the fiber.

TABLE 3				
Stabilized Fiber (SF) and Carbon Fiber (CF) Fabrication Conditions				
Fiber name	Tension during stabilization		Tension during carbonization	
	No	Yes	No	Yes
Stabilized fiber				
NSF	x			
TSF		x		
Carbon fiber				
NCFX*	x		x	
TCFX*		x		x
PCFX*		x	x	

*“X” is replaced by carbonization temperatures, varied from 500 to 1000.

The Dependency of CF Tensile Properties on Fiber Processing Conditions

[0135] The tensile properties of OL-based CFs produced using different fiber fabrication methods were compared

(FIGS. 8A-8B). Increasing carbonization temperature from 600 to 1000° C. led to monotonic increases of tensile strength and modulus for NCFs (i.e., thermal control-only fibers), which was contradictory to the temperature dependence observed for TCFs (i.e., the thermo-mechanically controlled fibers). However, tensile properties of NCFs were significantly lower, within the range previously reported for lignin-based CFs. This result confirmed that the thermo-mechanical control of lignin was responsible for the CF property improvement. Not only the tensile property values of CFs, but their dependency on carbonization temperature was also affected by the thermo-mechanical controlling. As described above, the tensile properties in the TCFs produced using either OL or OL/KL blends decreased when carbonization temperatures increased above 700° C. Among the three CFs produced using the same carbonization temperature of 800° C., PCF800 (i.e., thermomechanical controlling during stabilization only) had intermediate tensile properties between NCF800 and TCF800 (FIGS. 8A-8B). Specifically, tensile strength and modulus of PCF800 were 996 MPa and 76 GPa, compared to 2.12 GPa and 189 GPa for TCF800, and 549 MPa and 48 GPa for NCF800. This result clearly showed the importance of thermomechanical controlling during both stabilization and carbonization.

TEM Results of CFs Dependent on Processing Conditions

[0136] Transmission electron microscopy (TEM) analysis was performed on the selected CFs to visualize their nanostructures. In FIGS. 9A-9F, NCF700 and NCF1000 reveal amorphous carbons with randomly distributed nanocrystallites. Similar structures were reported for previous lignin-based CF (Johnson et al., "The Fine Structure of Lignin-Based Carbon Fibres," *Carbon* N. Y. 13(4):321-325 (1975), which is hereby incorporated by reference in its entirety). The branched and heterogenous molecules make it difficult for lignin to form a graphene structure. It has been reported that lignin does not graphitize even at temperatures above 2000° C. (Torres-Canas et al., "Improved Structure and Highly Conductive Lignin-Carbon Fibers Through Graphene Oxide Liquid Crystal," *Carbon* N. Y. 163:120-127 (2020), which is hereby incorporated by reference in its entirety). Unexpectedly, a turbostratic carbon structure was identified in TCF700 despite being produced at only 700° C. In TCF700, disordered graphene layers were stacked to form an orderly, onion-like structure. In comparison, turbostratic carbons in TCF800 were less curved. With increasing temperature, longer-ranged ribbon-like graphene layers were observed in TCF900 and TCF1000.

Analysis of SFs Produced Under Different Processing Conditions

[0137] The changes in the microstructures of lignin are the results of various chemical reactions that took place during the CF production process. The formation of turbostratic structure from lignin at such low temperatures without catalysts has been impossible previously, suggesting the thermomechanical controlling altered the ordinary chemical reactions and microstructural evolution from lignin. To support this statement, the chemical reactions and the microstructures were tracked by analyzing OL lignin-based fibers at different stages under different processing conditions.

Yields and Tensile Properties of SFs

[0138] TSF was obtained via a thermomechanically controlled stabilization, whereas NSF was prepared by a thermally controlled stabilization. Despite the heating profiles being identical for the two types of fibers, the yield of TSF was much lower than that of NSF (67% vs. 92%). Attributed to the increased mass loss and tension stretching, the average diameter of TSF was only 10 μm compared to 30 μm for NSF. On the other hand, the tensile strength and modulus of TSF were 340.6 MPa and 29.1 GPa, respectively, compared to 154.8 MPa and 4.7 GPa for NSF.

HSQC-NMR Results

[0139] HSQC-NMR spectroscopy was used to analyze the chemical structures of lignin, AF, TSF, and NSF. TSF and NSF stabilized up to 165° C. were analyzed here because the fibers stabilized at higher temperatures were only partly soluble in the solvent used for NMR analysis. FIGS. 10A-10H show the NMR spectra of lignin, AF and SFs at different C/H regions. The structure of AF shows the basic lignin functional groups since the melting spinning does not significantly change lignin structure (FIG. 10A-10D). In the oxygen-related regions (40-100 ppm/2.0-5.0 ppm of FIGS. 10C, 10E, and 10G), the cross-peaks of original lignin structures, including β -O-4, β -5, and resinol β - β structures (FIG. 10I) reduced in both TSF and NSF due to their bond cleavages during stabilization. The peaks at the aromatic region (100-160 ppm/5.0-8.0 ppm of FIGS. 10A, 10C, and 10E) also decreased in both fibers, which is related to the condensation of individual aromatic rings to fused rings. However, NSF and TSF had distinctively different molecular structures. Compared to NSF, there were significantly more bond cleavages for forming TSF. For example, the cross-peaks of C_α and C_β in β -O-4 can be observed in NSF, whereas they completely disappeared in TSF. While cross-peaks at the non-oxygen alkyl region (FIGS. 10B, 10D, and 10F) increased after stabilization, significantly more peaks were observed in TSF. Stilbene and secoisolaricresinol structures observed in this region were much more abundant in TSF. Stilbene structure originates from β -5, β -1, or β -O-4, formed upon the bond cleavages followed by rearrangements (Beste A., "ReaxFF Study of the Oxidation of Softwood Lignin in View of Carbon Fiber Production," *Energy and Fuels* 28(11):7007-7013 (2014), which is hereby incorporated by reference in its entirety). Secoisolaricresinol structure is derived from β -O-4, formed via homolytic cleavages at its C_β -O followed by coupling two C_β carbon radicals (Lahtinen et al., "Kraft Process-Formation of Secoisolaricresinol Structures and Incorporation of Fatty Acids in Kraft Lignin," *J. Agric. Food Chem.* 69(21):5955-5965 (2021), which is hereby incorporated by reference in its entirety). This structure can also be derived from resinol by cleaving its two symmetric C_α -O bonds. Two aromatic rings are connected via strong C-C or C-O bonds to form linear structures in both structures. Several new cross-peaks were only presented in TSF at this region, corresponding to aliphatic structures with CH or CH_2 at C_α and CH, CH_2 , or CH_3 at C_γ (Mattsson et al., "Using 2D NMR to Characterize the Structure of the Low and High Molecular Weight Fractions of Bio-Oil Obtained from LignoBoost™ Kraft Lignin Depolymerized in Subcritical Water," *Biomass and Bioenergy* 95:364-377 (2016), which is hereby incorporated by reference in its entirety).

Apparently, TSF had a molecular structure with significantly improved linearly containing abundant alkyl linkages. Such a structure cannot be formed by heating lignin alone.

FTIR Analysis Results

[0140] Functional groups of AF and SFs were also analyzed using FTIR. In FIG. 11, carbonyl groups (i.e., ketones, aldehydes, or carboxyls, peaks 4, 5 and 6) increased, whereas hydroxyl groups (peak 1) decreased in NSF. This increase in C=O groups was mainly due to oxidation at the aliphatic OH groups. Compared to NSF, the abundance of C=O and OH groups was lower in TSF. On the other hand, the peaks for alkyl stretching (peaks 2 and 3) and aromatic ring vibrations (peaks 7 and 8) were more pronounced in TSF than in NSF.

Fast Pyrolysis Results

[0141] The chemical structure of TSF was further investigated by pyrolyzing AF, NSF, and TSF (the gas chromatograms are shown in FIG. 12). Since fast pyrolysis can rapidly cleave organic bonds to fragmentize molecules, analyzing pyrolysis products can provide insights into the chemical structure of the original molecules. Pyrolysis of AF produced several phenolic monomers with aliphatic and oxygenated functional groups. These monomers are typical decomposition products of lignin formed when the aromatic side chains cleave. CO₂ and CO among the products are due to decarboxylation and decarbonylation of the side chain containing C=O groups. Phenolic monomers were nearly absent when NSF was pyrolyzed, indicating a highly condensed structure. On the other hand, NSF produced significantly higher amounts of CO₂ and CO than AF attributed to the increased C=O formation due to the oxidative stabilization. Unlike condensed NSF, TSF produced several phenolic monomers with methyl and ether groups, suggesting its structure is less condensed with fewer cross-linkages. TSF also produced fewer amounts of CO₂ and CO than NSF, which agrees with the FTIR result that TSF contains fewer C=O than NSF.

Raman Analysis Results

[0142] The above results showed that lignin undergoes a different set of chemical reactions during the thermomechanically controlled stabilization, resulting in a molecular structure that cannot be formed without such control. The microstructures of TSF and NSF were also analyzed to correlate with their different chemical structures. Raman spectra were analyzed at the cross-section and top views of the fibers so that their structural uniformity at different fiber directions could also be evaluated. In FIGS. 13A-13B, broad D and G peaks were observed in both TSF and NSF. While the D and G peak area ratio (I_D/I_G) usually represents the structural disorder in a graphitic material, stabilization of lignin does not form graphene structures. In amorphous carbon structures, I_D/I_G ratio is related to the abundance of benzene rings and side chain sp² carbons (Li et al., "FT-Raman Spectroscopic Study of the Evolution of Char Structure During the Pyrolysis of a Victorian Brown Coal," *Fuel* 85(12-13):1700-1707 (2006), which is hereby incorporated by reference in its entirety). The I_D/I_G ratios at the cross-section and top views of the fiber were 0.85 and 0.82 for TSF, while they were 0.80 and 0.71 for NSF. The higher I_D/I_G ratios in TSF indicate that the fiber contains higher

amorphous sp² carbons. D+D" peak was also found in TSF in both directions with similar relative peak intensities. In comparison, the D+D" peak was found only in the side-view spectra in NSF. This peak was previously reported in Raman spectra of highly oriented pyrolytic graphene, carbon nanotubes, or graphite paper (Shimada et al., "Origin of the 2450 cm⁻¹ Raman Bands in HOPG, Single-Wall and Double-Wall Carbon Nanotubes," *Carbon N. Y.* 43(5):1049-1054 (2005); Wang et al., "Anisotropic Thermal Conductivities and Structure in Lignin-Based Microscale Carbon Fibers," *Carbon N. Y.* 147:58-69 (2019), which are hereby incorporated by reference in their entirety). In graphite paper, the intensity of the D+D" peak was much stronger in its top view of the graphite than in the side view due to its anisotropic structure (Wang et al., "Anisotropic Thermal Conductivities and Structure in Lignin-Based Microscale Carbon Fibers," *Carbon N. Y.* 147:58-69 (2019), which is hereby incorporated by reference in its entirety). Therefore, the Raman results suggest that NSF structure is anisotropic, whereas TSF structure is isotropic in different fiber directions.

Effects of Thermo-Mechanochemistry on Lignin Stabilization

[0143] Since identical heating profiles were used to produce TSF and NSF, the differences in their chemical structures and microstructures described above are due to the tension control coupled with the thermal control during its stabilization. The results suggest that applying strong mechanical force to stretch the spun fibers undergoing thermal heating introduced the mechanochemistry of lignin in addition to ordinary thermochemistry. The coupled thermochemistry and mechanochemistry manipulated the conventional chemical reactions to transform lignin into a structure that cannot be formed by the thermochemistry of lignin alone. Mechanochemistry refers to reactions induced by a mechanical force applied to molecules, which can cause a distinct transformation compared to thermochemical reactions caused by evaluating temperature (De Bo G., "Mechanochemistry of the Mechanical Bond," *Chem. Sci.* 9(1):15-21 (2017); Li et al., "Polymer Mechanochemistry: From Destructive to Productive," *Acc. Chem. Res.* 48(8):2181-2190 (2015), which are hereby incorporated by reference in their entirety). The mechanochemistry of lignin is not well understood in literature, especially when it is coupled with thermochemistry. Previous studies showed that when lignin was ball-milled, the friction force could promote β -O-4 linkages in lignin (Dabral et al., "Mechanochemical Oxidation and Cleavage of Lignin β -O-4 Model Compounds and Lignin," *ACS Sustain. Chem. Eng* 6(3):3242-3254 (2018), which is hereby incorporated by reference in its entirety). Since ball milling was usually conducted at room temperature, the effect of thermochemistry was minimal. Here, mechanochemistry and thermochemistry can simultaneously play roles since strong tension was applied while the temperature of the spun fibers also increased. If lignin-spun fibers are stabilized without tension force or with an insignificant amount of tension force (which was the case for most of the previous lignin-based CFs), the chemical reactions of lignin would be driven solely by its thermochemistry. With increasing temperatures under an oxidative environment, heterogeneous side-chain functional groups in the aromatic rings of lignin are subjected to thermally induced bond cleavages, oxidation, repolymerization, and crosslinking in different fiber directions, leading to highly condensed

and non-oriented structures containing an increased number of C=O. The present results showed that coupling thermochemistry with mechanochemistry introduced novel thermo-mechanochemistry to promote increased bond scissions, rupturing the highly branched structures of lignin. Bond rupturing and chain fragmentation will disassemble the polymer structure (De Bo G., “Mechanochemistry of the Mechanical Bond,” *Chem. Sci.* 9(1):15-21 (2017), which is hereby incorporated by reference in its entirety). Thus, the bond cleavage effect alone is supposed to reduce the mechanical strength of TSF. However, as described above, TSF had much higher tensile properties than NSF. Thus, the effect of introducing thermo-mechanochemistry was more than deconstructing the heterogeneous polymer. During stabilization, the strong mechanical stress applied to the spun fibers in the fiber direction likely also directed the rearrangement and repolymerization reactions of the partly decomposed lignin structures containing reactive ends (i.e., radicals or functional groups). The deconstruction of the irregular and branched lignin structure followed by the mechanically controlled reconstruction of the dissembled structure in a defined fiber direction under thermal heating converted lignin into a novel structure with linearity in TSF, which cannot be achieved using thermochemistry of lignin. The new structure is also expected to consist of intra- or inter-molecular C—C or C—O linkages with high bond strengths aligned along the fiber axial direction because weaker bonds would not be able to survive the increasing temperature and the strong mechanical force simultaneously applied to the fibers. The weaker bonds of lignin (e.g., β —O—4) are likely eliminated and replaced by stronger bonds newly formed. In addition to bond scissions, other common reactions caused by mechanochemistry are pericyclic reactions and isomerization (Izak-Nau et al., “Polymer Mechanochemistry-Enabled Pericyclic Reactions,” *Polym. Chem.* 11(13):2274-2299 (2020), which is hereby incorporated by reference in its entirety). For example, stilbene cyclization may be promoted.

[0144] Mechanical stretching of the softening fiber also physically reduces fiber diameters during stabilization. The thinner fiber diameters of TSF can minimize heat transfer limitation during stabilization and promote greater and uniform oxygen penetration toward the fiber core compared to NSF with thicker fiber diameters. Thus, the fiber surface and core structures are expected to be more uniform in TSF than in NSF. Although the extent of oxidation is supposed to be greater in TSF than in NSF, TSF has a lower carbonyl content and total oxygen content than NSF (Table 4). The oxidation reactions in TSF likely promoted bond cleavages to release oxygenated volatile compounds and light gases rather than forming the end unit carbonyls. The yield of TSF was much lower than that of NSF, which supports that the increased bond scissions and rearrangements in TSF promote lightweight byproducts. The uniform structure with strong covalent bonds in TSF is expected to reduce the risk of mechanical failures within the fiber when an external force is applied to the fiber.

TABLE 4

Elemental Composition of AF, NSF, and TSF					
	C (%)	H (%)	N (%)	S (%)	O (%)
AF	67.403	5.063	0.253	0.044	27.236
NSF	64.890	3.293	0.297	0.078	31.442
TSF	64.990	3.366	0.350	0.051	31.243

Analysis of CFs Produced Using Different Processing Conditions

[0145] TSF and NSF were carbonized to various final temperatures using the same heating profiles described above but with different conditions for mechanical control. Different CFs were analyzed for their chemical and microstructural transformations during carbonization.

FTIR Results

[0146] In the FTIR spectra of CFs (FIG. 14), the peaks associated with aromatic rings (peaks 5, 6, and 7), carbonyls (peaks 3 and 4), and hydroxyls vanished in TCF700 and other TCFs obtained using higher carbonization temperatures. These structures disappeared because higher carbonization temperature promotes deoxygenation and cyclization reactions to form more fused benzene rings and nanocrystallites. Meanwhile, the intensity of the peaks representing the stretching vibrations of aliphatic C—H (peaks 1 and 2) increased in TCFs with increasing carbonization temperature up to 800° C. in TCF800. The new aliphatic groups formed at such high temperatures, suggest that the nanocrystallites or fused rings were interconnected through aliphatic linkages with high bond strengths in TCFs. In their turbostratic carbon structures, the aliphatic linkages could be present between graphene layers or at the edges of nanocrystallites. The aliphatic peaks started to decrease at TCF900 and TCF1000, likely because the linkages were either cleaved at higher temperatures or had undergone cyclic reactions. In comparison, the aliphatic peaks were either absent or weak in NCFs. The bands for aromatic ring vibration and carbonyls were visible even in NCF1000, suggesting a lower level of cyclization and higher oxygen bonding in the fiber when thermochemistry alone takes place.

XPS Results

[0147] The carbon-containing bonds in different CFs were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra are shown in FIGS. 15A-15D, and the quantified results are summarized in Table 5. The sum of —C—C and —C—H was 81.2% for TCF700. It became slightly lower for TCF800 and then increased for TCF900. On the other hand, the —O—C=O content decreased with increased temperatures to become negligible in TCF900. The —C=O content was lowest in TCF700 and increased at the fibers with higher carbonization temperatures. When compared with NCF800, TCF800 contained significantly fewer amounts of oxygen-bonded carbons. For example, the —O—C=O content was 22.3% in NCF800 whereas it was only 1.7% in TCF800. The results correspond to the FTIR results of CFs, indicating that introducing thermo-mechanochemistry can reduce oxygen-bonded carbons in CF. Oxygen-bonded carbons can hinder the growth of crystallites during carbonization (Kim, J. S. Roh, and M. S. Kim,

“Effect of Carbonization Temperature on Crystalline Structure and Properties of Isotropic Pitch-Based Carbon Fiber,” *Carbon Lett.* 21(1):51-60 (2017), which is hereby incorporated by reference in its entirety). Thus, the decreased oxygenated bonds are highly preferred for forming a graphene structure observed in TCFs.

TABLE 5

XPS Results of CFs				
CFs	—C—C—/—C—H (%)	—C—O— (%)	—C=O (%)	—O—C=O (%)
TCF700	81.20	3.02	8.66	7.12
TCF800	71.58	8.67	18.30	1.45
TCF900	84.49	2.96	12.55	0.0
NCF800	57.40	9.15	11.18	22.27

Raman Analysis Results

[0148] The Raman spectra of CFs were measured at the cross-section and top views (FIGS. 2A-2B). In FIGS. 2A-2B, the D and G peaks were broad due to the co-presence of graphene and disordered carbons, including amorphous carbons. Weak M and 2D peaks, representing graphene structures with ordered layers (Luo et al., “Enabling High-Quality Carbon Fiber Through Transforming Lignin into an Orientable and Melt-Spinnable Polymer,” *J. Clean. Prod.* 307:127252 (2021), which is hereby incorporated by reference in its entirety), appeared in the TCFs as the carbonization temperature increased. D+D" peak was observed in TCFs at similar relative peak intensities in both fiber directions. In comparison, D+D" peaks were negligible in NCF800 in both directions and much weaker in the cross-section view than in the top view of PCF800. Gaussian fitting was used to further analyze the D and G peaks (FIGS. 16A-16L). The I_D/I_G ratios of the CFs were calculated for two different directions (FIG. 2C). While I_D/I_G decreased in TCFs with increased carbonization temperature, the difference between the I_D/I_G at two different directions was the smallest for TCF700. Its Raman spectra distribution in the two directions was similar, implying its isotropic structure. As the carbonization temperature increased, TCF800 and TCF900 became more anisotropic as the difference of their I_D/I_G in two directions increased. As described above, the diameters of these fibers were larger than that of TCF700 due to stronger fiber shrinkage at higher carbonization temperatures. Thus, the increased anisotropic in these fibers is likely attributed to the fiber shrinkage and thicker fiber diameter. The increased anisotropic in TCF800 and TCF900 also correspond to the decreased tensile properties in these fibers. For the CFs produced using the identical carbonization temperature, the I_D/I_G decreased in the order of NCF800>PCF800>TCF800 in both directions. The decrease was much more obvious in the cross-section view of the fibers, suggesting that thermo-mechanochemistry can enhance the graphitization and ordering at both the surfaces and inner fibers to promote uniform CF structures. The extent of anisotropic was greatest with NCF800, followed by PCF800, and least with TCF800, which is the opposite order of their tensile properties. This result confirmed that the novel thermo-mechanochemistry introduced during stabilization and carbonization can greatly enhance the formation of graphene carbons and promote a CF structure with

greater isotropic. PCF800 had a greater structural disorder and much lower tensile properties than TCF800, highlighting the importance of thermo-mechanochemistry during carbonization.

XRD Results

[0149] The XRD equatorial scans of CFs were performed parallel and perpendicular to the fiber axis (FIGS. 17A-17B). The first band was broad in all CFs due to the convolution of (002) and γ bands. The γ band, which occurs at 2θ below 20° , is usually attributed to aliphatic side chains attached to the edge of nanocrystals (Sonibare et al., “Structural Characterization of Nigerian Coals by X-Ray Diffraction, Raman and FTIR Spectroscopy,” *Energy* 35(12):5347-5353 (2010), which is hereby incorporated by reference in its entirety). In NCF800, (002) and (100) bands were observed in both scans. Due to the random distribution of crystal plane orientations, two perpendicular crystal planes could be observed in both diffraction angles. In comparison, the (100) band was nearly absent in the parallel scans of TCFs. Although the appearance of both (100) and (002) bands in their perpendicular scans indicates that the crystals do not perfectly align, there was a preferred alignment in the fiber axial direction. Gaussian fitting of the XRD curves (FIGS. 18A-18H) was performed to calculate structural parameters, and the results are shown in Table 6. In TCFs, the crystallite sizes (L_a and L_c) increased whereas interlayer spacing (d_{002}) decreased along with increased carbonization temperature due to the growth of graphite carbons. The interlayer spacing of TCFs was larger than that of the perfect graphene structure (0.335 nm), due to aliphatic linkages between the layers. Compared to TCF800, NCF800 had larger-sized crystallites of larger interlaying spacing. However, these nanocrystals were randomly distributed without order, as shown in the TEM results. Crystalline ordering in TCFs, enabled by thermo-mechanochemistry rather than crystallite size, is likely more important for delivering high tensile properties in the lignin-based CF. Table 6.

TABLE 6

Structural Parameters of CFs Based on XRD Results				
	TCF700	TCF800	TCF900	NCF800
d_{002} (nm)	0.3675	0.3572	0.3516	0.3697
L_c (nm)	0.6155	0.8047	1.1003	0.9647
L_a (nm)	1.0725	1.2029	1.3434	1.9109

SAXS Analysis Results

[0150] Small-angle X-ray scattering (SAXS) analysis was performed to analyze pore sizes in CFs (FIG. 3). Table 7 lists the average pore diameters of different CFs calculated based on SAXS results. Along with other factors, the presence of fiber pores can significantly affect the mechanical properties of CFs. In addition to creating physical defects, the fiber pores hinder the growth of crystallites perpendicular to the graphene planes (Dun et al., “Investigation of Structural Characteristics of Thermally Metamorphosed Coal by FTIR Spectroscopy and X-Ray Diffraction,” *Energy and Fuels* 27(10):5823-5830 (2013), which is hereby incorporated by reference in its entirety). Large pores have stronger detrimental effects on mechanical properties than smaller pores since they can more easily introduce crack propagations

(Chambers et al., “The Effect of Voids on the Flexural Fatigue Performance of Unidirectional Carbon Fibre Composites Developed for Wind Turbine Applications,” *Int. J. Fatigue* 28(10):1389-1398 (2006), which is hereby incorporated by reference in its entirety). The pore size was much smaller for TCF800 than NCF800 (1.991 nm compared to 2.5 nm), indicating thermo-mechanochemistry also inhibited pore growth in CFs. As noted above, the thermo-mechanochemistry introduced during lignin stabilization promoted removing weak bonds and suppressed new carbonyl formation in TSF. If the weak bonds were not removed during stabilization, they would be cleaved during carbonization at higher temperatures to increase the amounts of gas byproducts, increasing pores in the solidified fibers. Carbonyls present in SFs are the source of CO₂ and CO gases during carbonization, contributing to fiber pores. Accordingly, removing the weak bonds and limiting carbonyl formation during stabilization is expected to reduce gas formation during the carbonization and, thus, inhibit pore growth in TCFs. It shows that the pore sizes of TCFs are strongly correlated with their carbonization temperatures, increasing with increasing temperature. The pore size was only 0.815 nm for TCF700, much smaller than that for TCF800 and TCF900. The turbostratic structure with interlocked disordered carbons, isotropic structure, and small pores in TCF700 are expected to prevent crack propagation of the pores beyond the limit for catastrophic failure from the extensive crystalline walls, leading to high tensile properties. As noted above, the tensile properties of TCFs were the highest with TCF700 and decreased with increasing carbonization temperature. Although the graphitization degree and crystalline size increased in the TCFs obtained with higher carbonization temperatures, they also had higher fiber diameters, anisotropic structures, and larger pore sizes. Crack propagation-induced mechanical failure is expected to be more pronounced under such conditions, resulting in decreased tensile properties in these fibers.

TABLE 7

Porosity Analysis of CFs Based on SAXS Results		
	b ¹	R ²
TCF700	0.2577	0.815
TCF800	0.6296	1.991
TCF900	0.6736	2.130
NCF800	0.7905	2.500

¹b (nm) is the Debye autocorrelation length of the pores

²R (nm) is the radius of the pore

The Role of Thermo-Mechanochemistry in Forming CF

[0151] During stabilization, thermo-mechanochemistry promoted the disassembly of the branched and irregular lignin structure to remove weak bonds and controlled the rearrangement reactions to enable orientated structure after stabilization. The new structure contained fewer oxygen-related bonds and more sp² hybridized carbons, which is also more isotropic than the structure generated by the thermochemistry of lignin. The results show that such a structure is readily graphitized using unprecedently low carbonization temperatures and produces fewer fiber pores during carbonization.

[0152] While the thermo-mechanochemistry introduced during stabilization could manipulate and modify ordinary thermochemical reactions of lignin to transform the irregular molecular structure into a much-desired structure in TSF, introducing thermo-mechanochemistry during carbonization was important in ensuring the evolution of ordered microstructures from TSF. During carbonization, a strong tendency for fiber shrinkage along the fiber direction was only observed with TSF. When the stabilization of lignin occurs in the absence of thermo-mechanochemistry, various functional groups could freely interact in random directions of the fiber to form highly crosslinked and non-oriented structures. Thus, carbonizing NSF does not show noticeable fiber shrinkage. TSF exhibited the shrinking tendency, suggesting the oriented molecular structure stretched along the fiber direction retains high chemical reactivity after stabilization. TSF was less crosslinked and condensed than NSF, implying that the strong tension force applied to the fiber mechanically restricted the freedom of the molecular structure to prevent the intermolecular bonds from developing crosslinking in undesired fiber directions. If TSF is carbonized in the absence or with insufficient mechanical restrictions, the functional groups remaining in the no-longer restricted structure could freely react in different directions, causing the fiber to shrink. Allowing the fiber shrinkage during carbonization will lead to a microstructure with increased structural disorder and anisotropic, eventually lowering the mechanical properties in CF. In comparison, applying sufficient high mechanical force to limit the fiber shrinkage will introduce thermo-mechanochemistry to ensure that the oriented structure of TSF crosslinks only at the desired fiber direction as it carbonizes, which was critical in forming ordered microstructures and graphene carbons in CF.

[0153] It has been previously considered that the non-oriented amorphous carbons and low-tensile properties of CFs are unavoidable with lignin precursors. However, results show that it is possible to overcome this challenging problem using a facile approach by controlling heat and mechanical force applied to lignin-derived fibers. Properly integrating thermal heating and mechanical stretching can introduce a novel thermo-mechanochemistry, which can manipulate ordinary chemical reactions to modify the molecular structure and control microstructural evolution, transforming lignin into an oriented structure with graphitized carbons. Present results suggest that structural ordering, isotropic structure, turbostratic carbons, and smaller pore sizes are critical in achieving high tensile properties in lignin-based CF. TCF700 had the highest tensile properties despite the extremely low carbonization temperature because the fiber could meet these critical factors, contributed by the newly introduced thermo-mechanochemistry. Unlike conventionally produced CFs, the tensile properties decreased at the TCFs produced at higher carbonization temperatures because the negative impacts caused by the increased anisotropic structure and larger pore size at these fibers were more prominent than the positive impact of the increased graphitization.

[0154] The TCFs of the present disclosure had both high tensile strength and modulus. Even for PAN-based CFs, carbonization temperatures above 1000° C. are usually required to obtain comparable tensile properties. The difference between PAN-based CF and lignin-based CF lies in their completely different molecular structures and reaction mechanisms for forming CF. PAN is a linear-chain polymer

without ring structures. Thus, PAN must form individual benzene rings from scratch through extensive cyclization during stabilization and carbonization. In comparison, lignin intrinsically owns benzene rings in their basic units. By introducing thermo-mechanochemistry during stabilization, the original randomly branched structure was reorganized into an oriented structure where abundant aliphatic bonds interconnect benzene rings. Such an aromatic structure with stable side chains makes it much easier to form a graphene structure than an ordinary lignin structure. Introducing thermo-mechanochemistry to ensure the ordered structures during the subsequent carbonization further enhanced its graphitization. Accordingly, graphitization can occur at a much lower temperature than the temperature required for PAN-based CFs, as confirmed by the abovementioned TEM results. In the lignin-based CF produced this way, turbostratic graphene structure and polyaromatic ring clusters are connected by strong aliphatic linkages, providing both strength and rigidity in the material.

Techno-Economic Analysis of Lignin-Based CF

[0155] The above results show that CFs with mechanical properties exceeding the DOE targets could be produced using sole lignin and melt spinning. A preliminary techno-economic analysis (TEA) was conducted to determine the cost of melt-spun lignin-based CF. The cost estimation was based on a 10,000 metric tonne per year facility, with a lignin purchase price of \$110/MT and a 10-hour stabilization time as the base case (equivalent to the case for the 80%/20% OL/KL-based CF in this work). Current and projected lignin-based CF costs were compared to a literature-estimated cost of PAN-based CF (FIG. 19) (Ellringmann et al., "Carbon Fiber Production Costing: A Modular Approach," *Text. Res. J.* 86(2):178-190 (2016), which is hereby incorporated by reference in its entirety). The results showed that the current production cost of lignin-based CF is estimated at \$4.17/lb, which is lower than that of the DOE automobile-grade CF. The impacts of techno-economic improvements on lignin-based cost projections were also studied. The cost can be reduced by lowering the lignin purchase price and increasing the plant capacity. Decreasing the lignin price to \$50/MT lower the CF cost by \$0.05/lb to \$4.12/lb, and increasing the plant capacity by 20% decreases the cost by \$0.19/lb to \$3.98/lb. On the other hand, decreasing the stabilization time from 10 hours to 5 hours decreased costs by \$1.25/lb to \$2.92/lb. As described above, the stabilization time is directly related to the precursor T_g . Extended stabilization hours were required in this work due to the low T_g s of the lignin precursors. A substantial reduction in stabilization time is expected when high T_g lignins are used.

[0156] The present disclosure describes the production of low-cost high-quality CFs using sole lignin without chemical treatment or additives. The property advancement is due to the introduction of thermo-mechanochemistry of lignin, which has been discovered for the first time. This novel chemistry can be introduced by properly integrating thermal heating and mechanical stretching and can transform lignin into oriented and graphene carbons by manipulating its chemical reactions and controlling the microstructure evolution. The proof-of-concept CFs have smaller fiber diameters than commercial CFs. However, CFs with higher tensile properties at industrial-relevant fiber diameters are expected in future work by employing the fiber fabrication system with precision control and further optimizing the

heating and tension profiles. The discovery of the thermo-mechanochemistry of lignin and the improved understanding of lignin-based CFs reported in this work provide critical knowledge for developing a facile and green approach to enable high-quality CFs from broader lignin. Low-cost lignin-based CFs will simultaneously address the demands for low-cost green CFs in industries and the biorefinery bottleneck on lignin valorization.

[0157] Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the claims which follow.

What is claimed:

1. A method of producing a lignin-based carbon fiber, said method comprising:

providing a lignin-containing material;

producing a lignin fiber from the lignin-containing material;

stabilizing the lignin fiber under tension, wherein the tension is adjusted during said stabilizing such that a maximum bearable tension is applied to the lignin fiber; and

carbonizing the lignin fiber under tension to produce a carbon fiber, wherein said carbonizing is carried out at a temperature below 1200° C. and wherein the tension during said carbonizing is adjusted to avoid shrinkage.

2. The method of claim 1, further comprising:

purifying the lignin-containing material prior to said producing a lignin fiber.

3. The method of claim 1, wherein said producing a lignin fiber is carried out by spinning the lignin-containing material.

4. The method of claim 3, wherein the lignin-containing material is spun using melt-spinning, wet-spinning, dry-spinning, or gel-spinning techniques.

5. The method of claim 3, wherein the lignin-containing material is spun at a temperature from about -60° C. to about 250° C.

6. The method of claim 1, wherein said stabilizing the lignin fiber is carried in an inert environment.

7. The method of claim 1, wherein said stabilizing the lignin fiber is carried in an oxidative environment.

8. The method of claim 1, wherein the tension applied during said stabilizing stretches fibers to a length greater than its length prior to said stabilizing.

9. The method of claim 1, wherein, during said stabilizing, the fiber is heated from a temperature of about 25° C. to a temperature of about 300° C. over 2-28 hours.

10. The method of claim 1, wherein said stabilizing is carried out while subjecting the lignin fiber to thermal treatment, plasma treatment, UV light treatment, or microwave radiation.

11. The method of claim 1, wherein said stabilizing is carried out at a tension of about 1.5 kPa to about 1250 kPa per fiber.

12. The method of claim 1, wherein said stabilizing is carried out at a temperature of about 105° C. to about 300° C.

13. The method of claim 1, wherein said carbonizing is carried out at a temperature of about 500° C. to about 1200° C.

14. The method of claim **13**, wherein said carbonizing is carried out at a temperature of about 500° C. to about 1000° C.

15. The method of claim **1**, wherein the carbon fiber has an average diameter of 2 μm to about 20 μm .

16. The method of claim **1**, wherein the carbon fiber has an average tensile strength of about 2.0 GPa to about 4.0 GPa.

17. The method of claim **1**, wherein the carbon fiber has an average tensile modulus of about 200 GPa to about 400 GPa.

18. The method of claim **1**, wherein the carbon fiber has inner pores having an average radius of about 0.2 nm to about 4.0 nm.

19. A carbon fiber prepared by the method of claim **1**.

20. The carbon fiber of claim **19**, wherein the carbon fiber has an average diameter of 2 μm to about 20 μm .

21. The carbon fiber of claim **19**, wherein the carbon fiber has an average tensile strength of about 2.0 GPa to about 4.0 GPa.

22. The carbon fiber of claim **19**, wherein the carbon fiber has an average tensile modulus of about 200 GPa to about 400 GPa.

23. The carbon fiber of claim **19**, wherein the carbon fiber has inner pores having an average radius of about 0.8 nm to about 2.2 nm.

24. A lignin-based carbon fiber comprising:

an elemental oxygen content of at least 1 wt %;

an elemental carbon content of at least 65 wt %;

an average diameter of about 0.1 μm to about 20 μm ;

an average tensile strength of from about 2.0 GPa to about 4.0 GPa; and

an average tensile modulus of from about 200 GPa to about 400 GPa.

25. The lignin-based carbon fiber of claim **24**, wherein the elemental oxygen content is from about 1 wt % to about 30 wt %.

26. The lignin-based carbon fiber of claim **24**, wherein the elemental carbon content is from about 65 wt % to about 88 wt %.

27. A molded article for a machine part, electric and electronic part, or automotive part, said article comprising: a matrix material; and the carbon fiber of claim **24** dispersed in said matrix material.

28. The molded article of claim **27**, wherein the molded article is an automotive part.

29. The molded article of claim **28**, where the automotive part is selected from the group consisting of a hood, a pillar, a panel, a structural panel, a door panel, a door component, an interior floor, a floor pan, a roof, an exterior surface, an underbody shield, a wheel component, a storage area, a glove box, a console box, a trunk, a trunk floor, a truck bed, a lamp pocket, a shock tower cap, a control arm, a suspension component, a crush can, a bumper, a structural rail, a structural frame, a cross car beam, an undercarriage component, a drive train component, and combinations thereof.

30. The method of claim **1**, wherein the carbon fiber has an average tensile modulus of about 50 GPa to about 500 GPa.

31. The carbon fiber of claim **19**, wherein the carbon fiber has an average tensile modulus of about 50 GPa to about 500 GPa.

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