

Title

## Worm-like carbon shell chains produced from wood

Text

Large-scale utilization of wood which command absolute majority in biomass for functional carbon precursors contributes to reduce greenhouse effect. Wood char generally has a limit on material usage because of non-graphitic structure<sup>1</sup>, so we developed a new functional wood char by iron-, or nickel-catalyzed carbonization, which has graphite-like structure with mesopores good for electroconductivity and liquid phase adsorption capacity for macro molecules<sup>2-5</sup>. However fine structure of the wood char is still not cleared. Here we report more than 70 wt % of iron-catalyzed wood char is filled with chained carbon shells formed by 3~20 defective stacking layers of carbon hexagonal planes, which look like nanometer-sized worms swarm. We name them “carbon shell chains”. The discussion of the formation mechanism reveals wood cell wall plays an important role for their efficient production. They are stable at 1800 °C under vacuum, but in air, burn under 600 °C, and are perfectly converted into hydrogen and carbon monoxide in a short time by steam at 900 °C. The control of their decomposition will bring out a new talent in the wood char as a big source of supply for nano-graphite or nano-graphene, which nanometer size and edge effects recently attract considerable attentions<sup>6</sup>. In addition, a simple and easy preparation of carbon shell chains implies they may be naturally produced on or in the earth rich in iron, and might give misinterpretation as nano-worms, though most of them may decompose into organic gases.

Utilization of woody biomass occupied more than 90 wt % of biomass has been world-widely researched since awareness of global warming by a massive release of carbon dioxide from fossil fuels. Above all, their thermochemical conversion to fluid fuels is featured by large-scale operation, but complicated structure of wood acquired through the long time evolution generally disturbs their full decomposition to gases or liquids to co-produce wood char unexpectedly<sup>1</sup>. The wood char which remains woody morphology has an amorphous carbon structure hardly to change graphitic structure even after high heat-treatment (see Supplementary Fig. S1 and S2a). This reason imposes some restrictions on their usages. Meanwhile we saw the advantages of the wood structure for water adsorption to design for metal ions highly dispersing into wood before carbonization, and succeeded in producing a new functional wood char

with graphite-like and mesoporous structure<sup>2-5</sup> (see Supplementary Fig. S2). However details of their fine structure are not clear yet. Here we report interesting results taken a leading part by electron microscopy.

As written in Method, we prepared iron-catalyzed wood char denoted by FeWC, which was obtained by 850 °C-annealing of wood char previously prepared by carbonization of iron loading wood at 500 °C (denoted by Pre-FeWC). FeWC can be directly prepared by carbonization of iron loading wood at 850 °C, too, but the former process is convenient for mass production. Some of FeWC were soaked into acid to remove catalytic metal (denoted by WC). A scanning electron microscopic (SEM) image of WC in Fig. 1a discloses countless nano-sized carbon filaments are closely packed in whole wood cell wall which framework still remains. Besides a high resolution transmission electron microscopic (HRTEM) image of WC in Fig. 1b indicates they have graphite-like structure. Obtaining more information about morphology of those filaments, partial oxidation in a muffle at 420 °C was conducted for WC to remove amorphous carbon (denoted by Ox-WC). As shown in Fig. 1c and d, the filaments were selectively left to appear in sight more clearly. Fig. 1e obtained from a flake of WC indicates both filaments of WC and Ox-WC are morphologically almost same. These images show they are winding chains with a length of 50-500 nm and formed by distorted carbon spheres with a diameter of 5-80 nm. Fig. 1b and scanning transmission electron microscopic (STEM) images of WC in Fig. 1f prove that all spheres are hollow, in other words, they are shells formed by 3-20 defective stacking layers of carbon hexagonal planes. Hereafter we call those filaments “carbon shell chains (CSCs)”. Their morphology is unique and looks as if nano-worms turn and wriggle.

In order to investigate how much CSCs actually occupy WC through thermo gravimetric analysis, in advance, WC was heated at 1800 °C under vacuum for 15 minutes (denoted HT-WC) to remove iron completely, because in spite of acid treatment, WC included around 1 wt % of iron with possibility of an active effect on oxidation. X-ray diffraction (XRD) profiles in Fig. 2a indicate that there are some peaks for Fe<sub>3</sub>C on FeWC and WC, and peaks for Fe<sub>2</sub>O<sub>3</sub> on Ox-WC, but any peaks for iron are not detected on HT-WC. Fig. 2b shows thermo gravimetric curves on FeWC, WC, Ox-WC and HT-WC with dot lines indicating oxidation temperatures of no metal loading wood char prepared in the same way as WC (denoted by NoWC), and then heated at 1800 °C in the same way as HT-WC (denoted by HT-NoWC). Both of them are amorphous carbon (see Supplementary Fig. S2a). Oxidation temperature of Pre-FeWC is 280 °C, too low to put down on the figure. FeWC loaded with about 9 wt % of iron burns at lower temperature than NoWC and the heaviest residue is left among all chars.

On the other hand, the last value of weight loss ratio on HT-WC, i. e., a hundred percent suggests that HT-WC contains no iron. It corresponds to the result from XRD analysis to confirm efficient removal of iron from WC. Two-steps oxidation is observed in early oxidation stage on HT-WC curve, where the first oxidation temperature is as same as that of HT-NoWC. The result implies that oxidation of amorphous carbon in HT-WC selectively breaks out ahead of CSCs, so the value of weight loss ratio at that time indicates a proportion of amorphous carbon. According to this presumption and a HT-WC yield from WC, about 90 wt %, it is estimated that more than 70 wt % of WC would be occupied by CSCs.

In view of the high production yield, CSCs seem to be easily obtained from wood. The formation mechanism is still under investigation, but there are some clues of elucidation such as the following results. (a) A HRTEM image of Pre-FeWC suggests high dispersion of iron particles with a diameter under 10 nm into the amorphous carbon matrix, shown in Fig. 3a. (b) HRTEM images of FeWC (see Supplementary Fig. S3) often show encapsulated iron particles with a diameter of 20~30 nm by stacking layers of carbon hexagonal planes. (c) XRD profiles of Pre-FeWC and FeWC in Fig. 2a explain iron behavior before and after formation of CSCs, where broad diffraction peaks for iron species appear on the former, but a few sharp peaks on the latter. (d) Nickel-catalyzed wood char also has CSCs which is morphologically about the same, but size of shells is larger and numbers of connected shells as a chain is less than those of iron-catalyzed wood char (see Supplementary Fig. S4). According to these results and many reports about shell carbons formed in gas or solid phase<sup>7-12</sup>, the mechanism is presumed as the following (Fig. 3b) : (1) the reaction starts with aggregation of fine metal particles dispersed into char during temperature elevating up to 850 °C, and (2) when they form a larger particle with a proper active size which each metal seemingly owns (Ni>Fe), the particle is encapsulated by a layer of carbon hexagonal planes through dissolution-precipitation of carbon with metal<sup>7</sup>, then the layer stacks thicker inwards by sequential nucleation of the layers at the metal-carbon hexagonal planes interface. (3) Thus, the metal is gradually forced to flow out of its self-produced capsule<sup>9,10</sup>, eventually expelled into amorphous carbon matrix connected to the carbon shell. (4) Repeating of a sequence of these reactions in wood cell wall produces a CSC. The key points of this hypothesis are formation of metal particles with a proper active size and a solid phase reaction space for producing CSCs. Considering that CSCs are obtained not only efficiently but easily from wood, wood could coincidentally have an ideal structure for CSCs formation. In other words, the unique hydrophilic structure of wood, such as multi-layers of cell wall formed by oxygen-containing components as cellulose,

hemicellulose and lignin<sup>13</sup>, could have an excellent capacity for trapping metal ion as a complex and make it possible for fine metal particles to disperse into relatively porous wood char through carbonization (see Supplementary Fig. S2). Of course, CSCs can be available from those wood components individually, but order of the yield is wood > cellulose  $\approx$  hemicellulose > lignin. Wood cell walls could behave not only as a material resource for carbon but also as a good reaction space for CSCs forming.

Stability of CSCs for some heat treatments is suggested in Fig.2. Sharp diffraction peaks at around 26 ° on WC, Ox-WC and HT-WC in Fig. 2a correspond to (002) plane of a graphitic lattice (correctly, not graphite but turbostratic carbon), are about the same on intensity, full-width at half maximum and interlayer distance, so it concludes stacking layers of CSCs to be stable after heat-treatment at 1800 °C under vacuum for 15 minutes, in the meantime, iron particles are all vaporized to be vacuumed. In air, Fig. 2b shows that FeWC burns easier than NoWC, but both of WC and Ox-WC, and HT-WC stand up harder than NoWC and HT-NoWC, respectively. Although CSCs are more bulky than NoWC because of their hollow shells and their stacking layers have many defects shown in Fig. 1b, crystal structure of CSCs prior to the bulky structure against airy oxidation. For steam gasification, steam treatment at 800 °C for 2 hours converted 24 wt % of FeWC mainly to hydrogen, methane and carbon dioxide, in short, only amorphous carbon in the char seemed to react with steam selectively. But the similar steam treatment at 900 °C quickly converted all carbon of FeWC mainly to hydrogen and carbon monoxide, and then magnetite is only left as a residue. Those productions are reminded of natural gas and Fischer-Tropsch process<sup>14, 15</sup> for synthetic liquid fuel as alternative petroleum. Anyway, if their decomposition is well controlled, FeWC and WC including a large quantity of nano-sized stacking layers of carbon hexagonal planes can supply inexpensive nano-graphite or nano-graphene, which is in the limelight for the nanometer size and edge effects<sup>6</sup>.

From simple process of CSCs production, it is assumed that they may be formed naturally on or in the earth with soaked wood in iron or nickel salt solution under hot atmosphere around 850 °C available from such as magma or impacts of meteorites. However it would be too hard to prove it, because most of them would change into gases and liquid, and if not, the size of CSCs would be too small to be found out in the usual way. By any chance, when a geologist comes across a worm-like material or a fossil with nanometer size, he must put about CSCs in his mind, because their shape shown in Fig. 1 associates him a worm or a bacterium indeed, such as a crystal of hydroxyapatite that was recently misunderstood as a nano-bacterium<sup>16</sup>.

## Methods

### Preparation of wood char

Powdered Japanese larch (*Larix leptolepis* GORD) with a particle size range of 0.50–1.40 mm was used as the raw wood material. As the iron precursor, iron nitrate was loaded onto raw wood by conventional aqueous impregnation. Loading of iron was adjusted to 3 wt % as iron in wood. After impregnation, excess water was removed in a rotary evaporator. A stainless vessel in which the iron loading wood was taken was placed in a vertical stainless tube reactor. The reactor was then electrically heated in a nitrogen flow to 500 °C and the temperature was maintained for 1h (Pre-FeWC). Then Pre-FeWC was heated again in the same condition up to 850 °C and the temperature was maintained for 1h (FeWC). Some of FeWC was soaked in 1M nitric acid for 24 h at room temperature followed by rinse with excess distilled water and dried at 100 °C (WC). Some of WC was air heated in a muffle at 420 °C until weight loss reached 30 wt % (Ox-WC), or heated at 1800 °C under vacuum for 15 minutes (HT-WC). As references, no metal loading wood char was prepared in the same way of FeWC (NoWC). NoWC was heated in the same way of HT-WC (HT-NoWC).

### Observation of wood char

Fig. 1a was obtained by JEOL JSM-6701F, and so forth on, Fig. 1b by FEI-Titan 80-300, Fig. 1c and d by JEOL JSM-6335F, Fig. 1e by Hitachi SU-8000, Fig. 1f by Hitachi S-5500, and Fig. 3a by JEOL Model 2000EX.

### Characterization of wood char

Thermo gravimetric analysis was conducted by ULVAC TGD 9600 for 15 mg of each char under the following conditions: heating at 2.5 °C/min up to 750 °C, through artificial air flowing at 80 cm<sup>3</sup>STP/min. X-ray diffraction profiles were obtained by RIGAKU RINT 1200 with radiation of Cu-K $\alpha$ . Steam gasification was investigated for 0.2 g of FeWC in a down drafting fix bed type reactor at 800 °C and 900 °C for 2 h through argon and steam (PH<sub>2</sub>O=0.5) flowing totally at 280 cm<sup>3</sup>STP/min. Gases were analyzed by TCD-gas chromatography.

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### **Author contributions**

K. Suzuki and T. Suzuki prepared and analyzed the wood chars. Y. Saito, H. Kita, K. Sato and T. Konno treated SEM and TEM imagery. K. Suzuki, Y. Saito and T. Suzuki wrote the manuscript.

Figure legends

**Figure 1 Observation of wood chars. (a) A SEM image of WC.** A framework of wood cell wall still remains after carbonization at 850 °C for 1h and the wall is closely packed with innumerable nano-sized carbon filaments. **(b) A HRTEM image of WC.** Graphite-like or turbostratic structure is observed everywhere, there 3~20 defective stacking layers of carbon hexagonal planes form warped round shapes. **(c) A SEM image of Ox-WC.** A framework of cell wall is almost broken and carbon filaments appear more clearly. **(d) A magnified image of (c).** Many distorted carbon spheres are meanderingly chained as a filament. They look like nano-worms swarming. **(e) A SEM image of a filament in WC.** It is taken at low acceleration voltage of 0.4 kV to avoid strong electron beam damaging the carbon. The shape really calls up a worm or a bacterium to mind. **(f) A secondary electron (left) and a bright field-STEM (right) images of WC.** Chained carbon spheres are all hollow, i. e., they are chained carbon shells formed by stacking layers of carbon hexagonal planes.

**Figure 2 Characterization of wood chars. (a) X-ray diffraction profiles of chars.** Broad peaks originated from iron are observed on a profile of Pre-FeWC. Sharp peaks on a profile of FeWC and small peaks on profiles of WC and Ox-WC, but no peaks on a profile of HT-WC are appeared for iron. High and sharp peaks at around  $26^\circ$  corresponded to graphite lattice (002) plane are about the same among WC, Ox-WC and HT-WC, although each char has a different thermal history. **(b) Thermo-gravimetric curves of chars.** No metal loading wood char prepared at 850 °C (NoWC) and NoWC heated at 1800 °C under vacuum (HT-NoWC) burn at 496 °C and 638 °C, respectively, they are illustrated by dot lines. FeWC included iron about 9 wt % burns at a lower temperature than that of NoWC. Two steps oxidation is observed on HT-WC curve, where first oxidation temperature corresponds to that of HT-NoWC as shown by an arrow.

**Figure 3 Presumption of the CSCs formation mechanism. (a) A HRTEM image of Pre-FeWC.** Dark spots of iron with a diameter under 10 nm highly disperse into amorphous carbon matrix. **(b) A model of the formation mechanism.** Reaction occurs inside of a wood cell wall field at all times. (1) Aggregation of fine iron particles. (2) Encapsulation of an active-sized iron particle by layers of carbon hexagonal planes. (3) Expulsion of iron from self-produced capsule to neighboring amorphous carbon area. (4) Repetition of a sequence of (2), (3) reactions.