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Microscopy and spectroscopy analysis of carbon nanostructures in highly fertile Amazonian anthrosoils

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ABSTRACT

The anthropogenic Amazonian soil "Terra Preta de Índio" (Amazonian Dark Earth) provides a potential model for a sustainable land-use system in the humid tropics. A large amount of carbon-based materials in this soil is responsible for its high fertility over long periods of usage, and soil scientists are trying to create "Terra Preta Nova" (New Dark Earth) by adding charcoal as a soil conditioner. By applying materials science tools, including scanning and transmission electron microscopy, energy dispersive X-ray, electron energy loss spectroscopy and Raman spectroscopy, we show that these millenary carbon materials exhibit a complex morphology, with particles ranging in size from micro- to nanometers, from the core to the surface of the carbon grains. From one side, our results might elucidate how nature solved the problem of keeping high levels of ion exchange capacity in these soils. From the other side, morphology and dimensionality are the key issues in nanotechnology, and the structural aspects revealed here may help generating the Terra Preta Nova, effectively improving world agriculture and ecosystem sustainability.

1. Introduction

The humid tropic is home to more than 4 billion people, many of which reside in developing countries. Soils in the humid tropics are characterized by low nutrient retention (Novotny et al., 2009) due to heavy rains and high temperatures. Even in tropical forests such as the Amazonian, the soil is poor and deforestation has led to desertification (Achard et al., 2002). Nevertheless, the pre-Columbian indigenous groups living in the Amazonian forest subsisted on agriculture in addition to hunting, fishing and gathering activities (Simões, 1982). Their way of life generated areas of highly fertile soil rich in plant nutrients known as "Terra Preta de Índio" (Amazonian Dark Earth) (Kern, 1996). This soil is dated up to 7000 years old, and it is generally accepted that they are anthropogenic in origin, although it is not clear whether this was intentional or was a byproduct of human activities (Smith, 1980). "Terra Preta de Índio" is more common in sites at the Amazon basin (Falcão et al., 2003; Glaser et al., 2002; Glaser, 2007; Marris, 2006), but it can also be found throughout the humid tropics and in other regions of South America and Africa (Blackmore et al., 1990; Zech et al., 1990).

The Amazonian Dark Earth sites are 20 ha on average (Glaser, 2007). While the soil in the fertile sites exhibit similar textures and mineralogy to adjacent soils, the key aspect of the fertile sites is the presence of approximately 70 times higher stable carbon content (Glaser et al., 2002). The presence of a large amount of carbon in the "Terra Preta de Índio" is responsible for the stability and recalcitrance of the soil organic matter (Cheng and Lehmann, 2009; Glaser et al., 2001; Liang et al., 2006; Novotny et al., 2009) and for a high soil cation exchange capacity (Liang et al., 2006), which has remained for thousands of years.

Researchers have proposed the production of "Terra Preta Nova" (new Amazonian Dark Earth) by adding charcoal as a soil conditioner to improve the cation exchange capacity, stability and recalcitrance (Glaser et al., 2002; Glaser, 2007; Marris, 2006; Novotny et al., 2009). In addition to the development of a more sustainable agriculture for the humid tropics, this process may increase the C sequestration in soil through a carbon negative release process, which may help prevent desertification. However, charcoal is a disordered, nano-structured carbon that can be produced of various sorts (Marris, 2006). Studies in the field of carbon-related materials have developed different types of well-defined and disordered structures

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Table 1
Composition details for the two "Terra Preta de Índio" sites explored in this work.

Sites	pH H_2O	pH KCl	K (Cmolc kg^{-1})	Ca	Mg	Al	t[a]	S[b]	Fe (mg kg^{-1})	Zn	Mn	Cu	P	V[c] (%)	M[d]
Serra Baixa (Iranduba)	5.77	4.43	0.10	3.06	0.51	0.15	3.82	3.67	59.00	15.90	72.90	5.00	214.00	96.07	3.93
Costa Laranjal (Manacapuru)	5.52	5.23	0.17	9.38	1.30	0.05	10.89	10.84	63.20	292.30	843.30	8.00	285.76	99.54	0.46

[a] t: effective cation exchange capacity (sum of K^+, Ca^{2+}, Mg and Al).
[b] S: basis sum (K, Ca and Mg).
[c] V: basis saturation percentage for effective cation exchange capacity.
[d] M: Al saturation percentage for effective cation exchange capacity.

(Boehm, 1994; Dresselhaus, 1998; Noorden, 2011). Here, we study the structure of the carbon materials found in "Terra Preta de Índio" (TPI), which we refer to as TPI-carbons, to elucidate their morphological aspects and the surface science behind their functionality. We show that TPI-carbons exhibit a special nanostructure that might be considered to generate "Terra Preta Nova" (TPN).

2. Materials and methods

The "Terra Preta de Índio" samples used in this work were collected near Manaus, Amazonas State, Brazil, from two sites: Serra Baixa (costa do Açutuba), Iranduba (Lat 3°30′S, Long. 60°20′W) and Costa do Laranjal, Manacapuru (Lat 3°18′33″S, Long. 60°33′21″W). Samples were taken from surface layer (0–20 cm depth) using a Dutch auger. Composition details are shown in Table 1. The charcoal samples were produced in the Charcoal Laboratory at *Instituto Nacional de Pesquisa da Amazônia* (INPA) from different plant species typical of this region: Ingá (*Ingá edulis* Mart.), Embaúba (*Cecropia hololeuca* Miq.), Lacre (*Vismia guianenses* Aubl. Pers) and Bamboo (*Dendrocalamus strictus*). The turf soil was from the Pau Branco mine in the state of Minas Gerais, Brazil.

The TPI soil samples were measured for extractable levels of potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P), iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) using the Mehlich 1 extraction (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}) (Kuo, 1996), with available P determined colorimetrically using the ammonium molybdate with ascorbic acid method (Braga and Defelipo, 1974). K determined by flame emission photometry, and Ca and Mg determined by atomic absorption spectrophotometry. Exchangeable aluminium with 1 mol L^{-1} KCl titrated with 0.025 mol L^{-1} NaOH. Fe, Mn, Cu and Zn were measured by atomic absorption spectroscopy. The soil pH was determined in water and KCl using an electronic pH meter with a glass electrode. Deionized water and KCl 1.0 mol L^{-1} were applied in the ratio of 1:2.5 soil:solution.

Ingá (*I. edulis* Mart.) biomass came from a 7-year-old tree, Embaúba (*C. hololeuca* Miq.) biomass from a 3-year-old tree, Lacre (*V. guianenses* Aubl. Pers.) biomass from a 4-year-old tree and Bamboo (*D. strictus*) biomass from a 10-year-old tree. Similar diameter woody materials were chosen and placed in the furnace. In the case of Ingá, the branches were used; for Lacre, Embaúba and Bamboo the middle of the tree trunk of the central stem was used, avoiding the base and top. The biochar was made from the fresh material in the pyrolysis furnace. The three combustion temperatures were 600 °C. Carbonization was accomplished in a pyrolysis furnace of refractory brick with a 20l capacity, reaching the temperature after a 2 h period. In sequence, the furnace was turned off and allowed to cool. After combustion, the samples were filtered with a 2 mm sieve.

Scanning electron microscopy (SEM) images were obtained using a Nova Nanolab 600 dual beam platform from FEI, and different samples were analyzed similarly, being acquired on the same equipment using 10 keV accelerating energy and 0.13 nA electron current. Selected grains were cut using a focused ion beam (FIB) in the same equipment, the ion bombardments being performed using a Ga^+ ion source working at 30 keV accelerating energy with an ion current of about 1.6 pA. Thin cross-sections were removed and welded onto a lift-out copper grid for subsequent analyses. As described further, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX) microscopy and spatially localized electron energy loss spectroscopy (EELS) were performed on a Cs-corrected FEI Titan 80/300 transmission electron microscope, equipped with a Gatan imaging filter Tridiem and an EDX analyzer. The EELS spectra were collected using an electron monochromator, reaching an ultimate energy resolution of 0.2 eV. The spectroscopic techniques (EDX and EELS) were performed in STEM mode, allowing nanometer scale spatial resolution. The elemental mappings were obtained by integrating characteristic X-ray signals during a drift-corrected STEM spectrum imaging experiment. STEM images were acquired using a high-angle annular dark-field detector.

Raman scattering measurements were performed in the TPI-carbons with the following: (1) an Andor™ Tecnology-Sharmrock sr-303i spectrometer, coupled with a charge-coupled device (CCD) detector in the backscattering configuration using a 60× objective lens and a 632.8 nm He–Ne excitation laser and (2) a T64000 Horiba Jobin-Yvon spectrometer coupled with a charge coupled device (CCD) detector in the backscattering configuration using a 50× objective lens and both 514.5 nm and 488.0 nm laser lines from an Ar^+ laser. For statistical analysis, the samples were measured as received, deposited on a cover slip, and after dissolution in DI water, a drop being placed onto an individual cover slip and measured after it dried. Furthermore, a randomly selected TPI-carbon grain was sectioned in a way that the exposed interface was turned to a cover slip, and spatially localized Raman spectra were obtained from the interior (core) and the exterior (surface) regions. The charcoal and turf samples were also characterized with Raman spectroscopy. To fix the samples on a glass cover slip, droplet-sized amounts of samples were deposited on deionized water drops on the cover slip and let dry.

3. Results and discussion

Fig. 1(a) shows a typical scanning electron microscopy (SEM) image of a randomly collected TPI-carbon grain, which measures on a scale of a few 100 μm. Various grain shapes were observed and were generally nonspherical, which is in agreement with a biochar origin (Stoffyn-Egli et al., 1997).

Conventional transmission electron microscopy (TEM) analysis of the TPI-carbon cross-sectioned slices showed two topologically distinct zones (see Fig. 1(b)). One zone demonstrated continuous contrast, was microns in scale, and composed the bulk grain core. The other zone exhibited a submicron porous structure formed by assembling 10–1000 nm particles that were located on the external part of the grain and composed the grain surface. A scanning transmission electron microscopy (STEM) image of a