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Magnetism in disordered carbon as a function of the extent of graphitization

K. Govind Raj [a,b], P.A. Joy [a,b,*]

[a] Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, India
[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-National Chemical Laboratory, Pune 411008, India

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ABSTRACT

Magnetic properties of disordered carbon have been investigated as a function of the extent of graphitization. It is found that the magnetization of the disordered carbon decreases with increasing degree of graphitization. Treatment with acid modifies the magnetic characteristics considerably and the original magnetic characteristics are retained upon further heat treatment. The results show that the intrinsic magnetic behavior of the disordered carbon depends on the microstructure and that the edge states play a critical role in deciding the magnetic interactions in the amorphous carbon system.

1. Introduction

Carbon based materials containing only s and p electrons and exhibiting ferromagnetism are promising candidates for various magnetic applications due to their low cost and light weight. There are many studies reported in the literature on the magnetic characteristics of carbon derived from various resources [1]. Magnetic properties observed in carbon based materials have been ascribed to the electronic properties arising from mixed sp^2–sp^3 sites and peculiar edge states [2]. Magnetic response of carbon structures is found to be highly dependent on their microstructure and the presence of heteroatoms in the carbon network or guest molecules between the graphitic layers or inside the pores [3–5]. These observations are in good agreement with theoretical predictions [6,7]. Extinction of ferromagnetism and development of diamagnetic character in highly oriented pyrolytic graphite (HOPG) after annealing at very high temperatures, due to the increase in grain size and reduction of edge states, point towards the importance of grain boundary, defects or vacancies [8]. Irradiation dosage dependent magnetic ordering in proton irradiated HOPG [9] and nanodiamond [10] irradiated with ^{15}N and ^{12}C also have established the role of defects towards creating a magnetic microstructure. Moreover, the observation of a spin-glass like state in different carbon nanosystems, due to the complex interactions among isolated spin clusters, is of particular interest for studying the development of magnetic interactions in the carbon based materials [11–13].

Most of the studies reported on the magnetic properties carbon are performed on ordered carbon allotropes with relatively high crystallinity. Here we report magnetic properties of amorphous carbon which is more disordered than those studied previously, so that more clarity can be brought to the magnetism in disordered carbon which is easily processable than the ordered allotropes.

2. Experimental section

Amorphous carbon was prepared by the pyrolysis of a coconut shell. A dry coconut shell was crushed into small pieces ($\sim$10 mm $\times$ 10 mm) and pyrolyzed at different temperatures in the range 500–1000 °C, in a horizontal programmable tubular furnace under a flowing nitrogen atmosphere. The temperature of the furnace was kept constant at the desired heat treatment temperature (HTT) for 4 h and further cooled to ambient temperature. The brittle carbon pellets thus obtained were powdered using an agate mortar and a pestle. The as-pyrolyzed samples were treated with concentrated HCl at 80 °C for 24 h and all the acid treated samples were recovered by filtration and washed several times using double distilled water.

The samples heat treated at different temperatures are labeled as HTxxx and the acid treated samples are labeled as HTxxxA, where xxx is the pyrolysis temperature. To check the efficiency of the acid extraction process, HT500A obtained after washing HT500 with acid was again subjected to acid treatment and analyzed for impurities and the carbon material thus obtained is labeled as HT500A1.

Powder X-ray diffraction (XRD) studies were performed on a Phillips X'pert pro diffractometer using Cu Kα radiation. Raman

* Corresponding author. Tel.: +91 20 2590 2273; fax: +91 20 2590 2636.
E-mail address: pa.joy@ncl.res.in (P.A. Joy).

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spectra were recorded on a Horiba JY labraman HR 800 micro Raman spectrometer using 633 nm He–Ne laser. Quantitative determination of impurities were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis on a Spectro Arcos FH-12 analyzer. Magnetic measurements were performed using a Quantum Design MPMS 7T SQUID VSM and the data were corrected for diamagnetic background signal from the sample holder.

3. Results and discussion

Pyrolysis of the coconut shell above 400 °C is known to induce carbonization and further increase in the heat treatment temperature leads to ordering of amorphous carbon by removal of dangling bonds and heteroatom containing terminal groups [14,15]. XRD patterns (Fig. 1) of the pyrolyzed samples consist of two broad peaks corresponding to the (002) and (100) Bragg reflections of amorphous carbon. The in-plane (L_a) and out-of-plane (L_c) coherence lengths were calculated from the FWHM of the (100) and (002) peaks respectively [16,17]. With the increase in HTT from 500 to 1000 °C, L_a is found to increase from 15 to 20 Å, and L_c increases from 12 to 16 Å.

Raman spectra (Fig. 2) of the different samples consist of two peaks due to graphitic G peak at $\sim 1575\ cm^{-1}$ corresponding to the in-plane bond stretching motion of sp^2 carbon atoms and the D peak at $\sim 1335\ cm^{-1}$ which will be absent in a perfect graphitic structure and appears only in the presence of structural disorder. For carbon based materials, depending on the extent of graphitization, intensity ratio of D-peak to G-peak, $I(D)/I(G)$, is reported to follow different trends with L_a, where $I(D)/I(G) \propto L_a^{-1}$ and $I(D)/I(G) \propto L_a^2$ for graphitic and amorphous carbon, respectively [18–21]. This change over in the dependency of $I(D)/I(G)$ with L_a occurs through a broad maximum. For the present pyrolyzed samples (Fig. 3) the Raman G peak position initially increases sharply and then decreases slowly after reaching a maximum value, with the increase in HTT. Similarly, as shown in the inset of Fig. 3, $I(D)/I(G)$ ratio initially increases sharply as L_a is increased

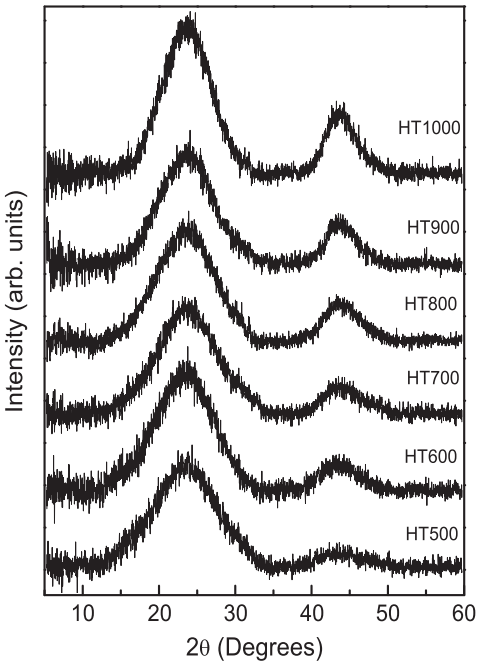

Fig. 1. Powder XRD patterns of the as-pyrolyzed carbon samples.

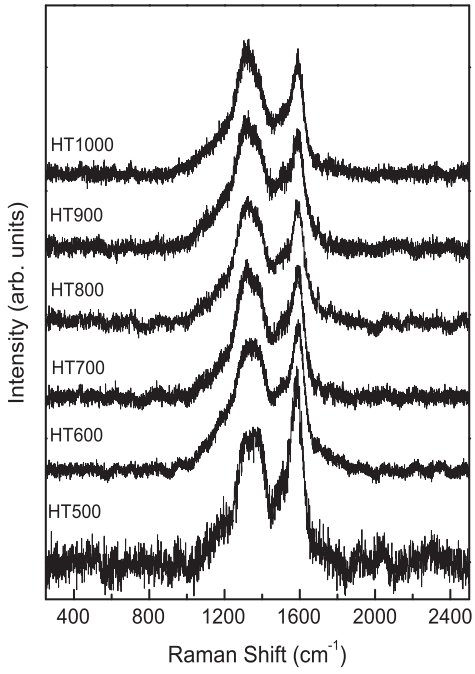

Fig. 2. Raman spectra of the as-pyrolyzed carbon samples.

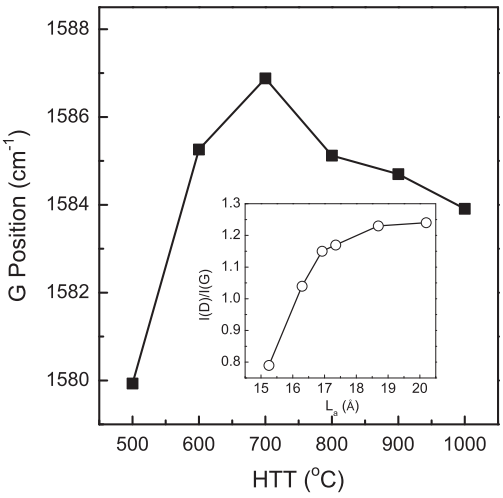

Fig. 3. Variation of the Raman G peak position as a function of heat treatment temperature. Inset: variation of the $I(D)/I(G)$ ratio as a function of L_a.

and reaches a broad maximum at higher L_a values close to 20 Å. These observations indicate the transition from amorphous carbon to nanocrystalline graphite. Thus, the present samples are in the boarder region separating the two carbon forms and hence does not obey the above given relations.

Quantitative determination of impurities in pyrolyzed samples performed by ICP-OES after acid extraction showed that apart from the ferromagnetic elements Fe, Co and Ni in trace amounts (< 100 ppm), many non-magnetic elements are also present which include K (~ 600 ppm), Ca (~ 350 ppm), Na (~ 300 ppm), Al (~ 200 ppm) and B (~ 100 ppm). The efficiency of the acid extraction process in removing the magnetic impurities was verified by a second acid treatment on HT500A and further ICP analysis. The ICP analysis showed < 5 ppm each of Fe, Co and Ni, indicating complete removal of the magnetic impurities after the first stage extraction itself. There is not much change in the Raman spectra and the XRD pattern of HT500A compared to that of HT500 (Fig. 4) which rules out any major changes in the carbon microstructure on acid treatment.