Ferromagnetic amorphous carbon derived from low molecular weight organic compounds

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Recently ferromagnetic signals have been observed in host of carbonaceous materials. In this paper, we report that the simple combustion products of low-molecular weight aromatic compounds like toluene and naphthalene clearly show ferromagnetic signals at 300 and 10 K with coercivity as low as ≈70 Oe and -100 Oe at 300 K and 10 K respectively and saturation magnetization as high as 5.1 × 10⁻⁴ and 5.5 × 10⁻⁴ emu at 300 K for toluene and naphthalene carbon respectively. These materials have been found to be air-stable at room temperature and they do not strictly obey Curie-Weiss law. The combustion products were characterized with the aid of Magnetometric studies, FTIR, SEM and TEM. Atomic absorption spectrophotometric analysis reveals that among ferro/ferrimagnetic contaminants, only iron is present in such a low concentration that it cannot account for a saturation magnetization as high as 5.5 × 10⁻⁴ emu. Hence, the origin of ferromagnetism is partly intrinsic in nature.

It was theoretically predicted as early as in 1968¹ that ferromagnetic signals may be observed in carbonaceous materials, but very recently it has been experimentally observed in elemental carbon as well as in carbonaceous materials. This aroused great amount of interest and skepticism among material scientist and physicists. Esquinazi et al.² observed ferromagnetic signals in highly oriented pyrolytic graphite (HOPG). Prior to that pyrolysis product of adamantane (tricyclo[1,1,3,3]decane) via vapour deposition was reported to show ferromagnetic signals³. Rode et al.⁴ reported unconventional magnetism in all types of carbon nano-foams. Irradiation of carbon films by proton beams was found to produce micrometer-sized magnetic spots⁵. Gonzales et al.⁶ have theoretically shown that some topological defects in graphene sheets may lead to ferromagnetism. Very recently, Ohldag et al.⁷ have observed that spin polarization of π-electrons are responsible for the intrinsic ferromagnetism in metal free carbon films irradiated with proton beams. However, any acceptable theory is still elusive for ferromagnetism in hydrogenated amorphous carbon (herein after referred to as a-C:H).

Taylor et al.⁸ have reported formation of C₆₀ and C₇₀ fullerenes by the pyrolysis of naphthalene at about 1000°C. The microstructure of the dehydration products of certain carbohydrates has been studied by Dasgupta⁹,¹⁰ and observed carbon nanorods in sucrose char obtained by the action of H₂SO₄, but these materials were, as expected, diamagnetic in nature. Dasgupta and Deb Ghosh¹¹ have shown that the structure of a-C:H obtained by the combustion of benzene, changes considerably on prolong sonication. The benzene carbon was found to be at least paramagnetic in nature. Herein we report, that the simple combustion of toluene and naphthalene at much lower temperature (at their respective ignition temperature) yields hydrogenated amorphous carbon, which show clear ferromagnetic signals (hysteresis) of very small coercivity and those are by no means fullerenes, confirmed by electron diffraction, FTIR and solubility studies.

Experimental Procedure

Material preparation

About 50 mL of toluene was taken in a clean and dried spirit lamp and made to burn. The wick of the spirit lamp was washed with acetone and subsequently dried prior to the process of combustion. A clean silica crucible (25 mL capacity) was held just above the flame to collect the combustion product.

In case of naphthalene, a previously cleaned wick was fixed in molten naphthalene at 70°C and a candlestick of naphthalene was made within a glass container and this candle was made to burn. The

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combustion products were collected in a similar fashion on a silica substrate.

**SQUID magnetometric measurement**

20 mg of each sample were wrapped in a 2×2 inch teflon sheet and inserted into Quantum Design SQUID Magnetometer (model No:MPMXL) holder. Prior to that the magnetometer was properly aligned. The SQUID magnetometer was provided with a solenoid that can generate a magnetic field of 5 tesla. The magnetometer response enables measurement of samples with a minimum magnetic moment of $5 \times 10^{-8}$ emu. We have opted for 4 cm scan length for magnetization measurement. The plot of applied field (in Oe) versus magnetization (in emu) were recorded for both the samples at 10 and 300 K along with the plot of DC magnetization as a function of temperature (in Kelvin).

**TEM studies**

10 mg of each of carbon samples from naphthalene and toluene were dispersed separately in 5 mL A.R. grade ethanol and sonicated for 10 min. Then the dispersions were 4 times diluted. One drop of each diluted dispersion was taken in two separate carbon coated 300 mesh copper grid and subsequently bright field micrographs were recorded in a 200 kV JEOL transmission electron microscope (model No:JEM201). Selected area electron diffraction diagrams (SAED) were also recorded in a CCD camera.

**EDS and SEM studies**

The SEM diagrams of both the samples were recorded in a JEOL field emission scanning electron microscope (Model No: JSM6700F). Elemental composition for both the samples were obtained with the aid of energy dispersive spectroscopic (EDS) technique.

**Atomic absorption spectrophotometric studies**

25 mg of each carbon samples derived from toluene and naphthalene respectively were digested in 15 mL of conc. nitric acid (A.R. grade) and evaporated to dryness. This is repeated for three times. Then 100 mL of deionised water was added to each dried residue and shaken well. These solutions were subjected to atomic absorption spectrophotometric (Perkin Elmer, Analyst 100) analysis to estimate the amount of ferro/ferrimagnatic contaminants present in it (viz. Fe, Co and Ni or their compounds). Prior to that 15 mL of blank conc. HNO$_3$ was digested and evaporated to dryness to assess the amount of these metals present in the nitric acid used for digestion.

**FTIR studies**

About 3 mg of each samples were mixed with 300 mg of FTIR grade KBr and subsequently pellets were prepared. FTIR spectra of these pellets were recorded in a Nicolet FTIR spectrophotometer (Model No:IR Magna750) with 4 cm$^{-1}$ resolution. Prior to that 50 scans were co-added.

**Results and Discussion**

**Magnetometric studies**

Figures 1 and 2 show applied field versus magnetization curves for both the samples at 300 and 10 K respectively. At 300 K both the samples gave
a saturation magnetization in the order of $1 \times 10^{-4}$ emu or 0.0255 emu$^{-1}$ (that of magnetite, i.e., Fe$_3$O$_4$ is 30.6 emu$^{-1}$) and very small coercivity (~70 Oe). While at 10 K saturation magnetization goes down negligibly and the coercivity increases (~100 Oe). It naturally follows that the Curie temperature of both the samples lie above 300 K. However, no correction due to diamagnetic contribution of the sample holder and that of the teflon sheet that wraps the sample could be incorporated in any cases.

It is noteworthy that the saturation magnetization is almost independent of temperature in the range of 10 to 300 K. In case, entire magnetisation results from any ferromagnetic contaminants like γ-, Fe$_2$O$_3$, Fe$_3$O$_4$ etc., such behaviour is quite unlikely.

Figure 3 shows plot of inverse of DC magnetization (emu$^{-1}$) as a function of $T$ (K). It was found that these plots deviates from linearity and hence do not obey Curie-Weiss law. No commonly known ferri or ferromagnetic contaminants are known to behave like a non-Curie-weiss magnet below Curie temperature.

The saturation magnetization increases very slowly at the rate of $1.30775 \times 10^{-7}$ emu/K, as the temperature goes down. This is also in contrary to the behavior of any known ferro/ferrimagnets.

**TEM and electron diffraction studies**

Figure 4 shows the electron diffraction diagrams of both the samples. Electron micrograph of both the samples were of similar nature, depicting 3D entangled carbon network made up of nearly spherical globules (of 50-80 nm in diameter).

Electron diffraction diagrams of both the samples show essentially two rings, one broad and corresponding to $d_{002}$ line of graphite ($d \approx 3.37$ Å) followed by another sharper ring at higher angle. Table 1 shows the inter-planner distances corresponding to observed rings (to be precise hallows). As the carbon content of the parent molecule increases, the $d_{002}$ value approaches 3.37 Å, which is the $d_{002}$ value of graphite suggesting higher degree of graphitisation is attained with the increase of carbon content of the parent molecule.

Since the coercivity is so small, near ~70 Oe, we looked for nano clusters of Fe containing compounds, which might give rise to single domain ferro/ferrimagnets responsible for so small coercivity. No other material could be detected in the electron micrograph. Several selected area electron diffraction diagrams were recorded at random but neither
Laue spot nor any characteristic line could be seen by virtue of which we could ascertain the presence of ferro/ferromagnetic contaminants of nano size.

**SEM and EDS studies**

Figure 5 shows the SEM diagram of both the samples. The 3-D globular carbon network is clearly evident. EDS study confirms the absence of any ferromagnetic contaminants. Only carbon and oxygen were detected. Table 2 shows the elemental composition of both the samples. Fe could not be detected. True, the detectibility limit of Iron using EDS technique is about 100 ppm\(^{12}\). However, it is very difficult to detect presence of Fe using EDS technique when these are entrapped within the carbon matrix.

**Atomic absorption spectrophotometric studies**

Detail results of the atomic absorption spectrophotometric analysis are depicted in Table 3. It is evident from Table 3 that Ni and Co are absent.

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**Table 1**

<table>
<thead>
<tr>
<th>Line No.</th>
<th>Interplanner distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.628 nm</td>
</tr>
<tr>
<td>2</td>
<td>2.155 nm</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon (%)</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene carbon</td>
<td>98.41</td>
<td>1.59</td>
</tr>
<tr>
<td>Toluene carbon</td>
<td>97.88</td>
<td>2.12</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ni (mg/L)</th>
<th>Co (mg/L)</th>
<th>Fe (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanc HNO(_3)</td>
<td>0.008</td>
<td>Nil</td>
<td>0.076</td>
</tr>
<tr>
<td>Toluene carbon</td>
<td>0.008</td>
<td>Nil</td>
<td>0.139</td>
</tr>
<tr>
<td>Naphthalene carbon</td>
<td>0.0089</td>
<td>Nil</td>
<td>0.141</td>
</tr>
</tbody>
</table>
The concentration of Fe is 0.139 mg/L and 0.141 mg/L for toluene and naphthalene carbon respectively. The blank nitric acid was found to contain 0.076 mg/L of Fe. Therefore in 100 mL aq. extract derived from 25 mg toluene carbon, Fe present:

\[0.0139 - 0.0076 = 0.0063 \text{ mg of iron}\]

20 mg of carbon contains = 0.00504 mg Fe

We have chosen 20 mg, since we inserted 20 mg of samples in the SQUID magnetometer.

If the entire magnetization contribution comes from a contaminant, say $\gamma$-Fe$_2$O$_3$ let us try to calculate its contribution.

0.00504 mg comes from (160/112) × 0.00504 $\gamma$-Fe$_2$O$_3 = 7.2 \times 10^{-3}$ mg of $\gamma$-Fe$_2$O$_3$

Saturation magnetization for $\gamma$-Fe$_2$O$_3$ at 300 K is 60 emu/g.

Therefore, $7.2 \times 10^{-3}$ mg of $\gamma$-Fe$_2$O$_3$ would give rise to $(60/1000) \times 7.2 \times 10^{-3}$ emu = $4.32 \times 10^{-4}$ emu

In case of toluene carbon we obtained a saturation magnetization of $5.1 \times 10^{-4}$ emu, more than what is expected.

In case of naphthalene carbon $5.2 \times 10^{-3}$ mg Fe was found to be present in 20 mg of carbon sample.

This would lead to a magnetization of $4.4 \times 10^{-4}$ emu, (in case the contaminant is $\gamma$-Fe$_2$O$_3$) which is by far less than what we obtained for naphthalene carbon, i.e., $5.5 \times 10^{-4}$ emu.

Magnetite (Fe$_3$O$_4$) on the other hand has a saturation magnetization 30.6 emu g$^{-1}$ at 300 K. If the entire magnetic contribution comes from magnetite, 0.00504 mg would give rise to a saturation magnetization of $4.17 \times 10^{-4}$ emu in case of toluene carbon and $4.32 \times 10^{-4}$ emu in case of naphthalene carbon, which are again by far less than what we have observed.

Other ferromagnetic contaminants, such as metallic iron, metal ferrites etc, are extremely unlikely to be present in the flame of toluene or naphthalene.

Hence, we deduce that origin of ferromagnetism in these materials is partly intrinsic in nature.

**FTIR studies**

Figure 6 shows the FTIR spectra of toluene and naphthalene carbon in the region of 2800-3100 cm$^{-1}$. Table 4 shows the bands observed in the FTIR spectra of these two carbon samples along with their assignments according to Dishler et al. to different vibrational modes. It is evident from Table 4 that sp$^3$CH$_2$ (sym & asym) stretching modes and sp$^3$CH(arom) modes are present. The band due to sp$^2$CH(arom) is so weak, particularly in toluene.

**Table 4 – (a) FTIR bands observed in naphthalene carbon in the range of 2800-3100 cm$^{-1}$**

<table>
<thead>
<tr>
<th>Band No.</th>
<th>Band position (cm$^{-1}$)</th>
<th>Nature</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2823.15</td>
<td>Broad</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>2854.05</td>
<td>Strong, sharp</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>3.</td>
<td>2886.34</td>
<td>Broad, weak</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>4.</td>
<td>2921.28</td>
<td>Strong, sharp</td>
<td>sp$^3$CH$_2$(y)</td>
</tr>
<tr>
<td>5.</td>
<td>2952.05</td>
<td>Shoulder</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>6.</td>
<td>2981</td>
<td>Weak</td>
<td>sp$^3$CH$_2$(olef)</td>
</tr>
<tr>
<td>7.</td>
<td>3009</td>
<td>Weak</td>
<td>sp$^3$CH$_2$(olef)</td>
</tr>
<tr>
<td>8.</td>
<td>3040</td>
<td>Weak</td>
<td>sp$^3$CH$_2$(olef)</td>
</tr>
<tr>
<td>9.</td>
<td>3071</td>
<td>Weak</td>
<td>sp$^3$CH$_2$(olef)</td>
</tr>
</tbody>
</table>

(b) FTIR bands observed in toluene carbon in the range of 2800-3100 cm$^{-1}$

**Table 4 – (b) FTIR bands observed in toluene carbon in the range of 2800-3100 cm$^{-1}$**

<table>
<thead>
<tr>
<th>Band No.</th>
<th>Band position (cm$^{-1}$)</th>
<th>Nature</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2855</td>
<td>Strong, sharp</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>2.</td>
<td>2923</td>
<td>Strong, sharp</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>3.</td>
<td>2970</td>
<td>Shoulder</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
<tr>
<td>4.</td>
<td>3050</td>
<td>Weak</td>
<td>sp$^3$CH$_2$(sym)</td>
</tr>
</tbody>
</table>

Fig. 6 – FTIR spectra of (a) toluene and (b) naphthalene carbon in the range of 2800-3100 cm$^{-1}$. 
carbon, a $2^{\text{nd}}$ derivative of the spectra (Fig. 7) was generated, which clearly depicts presence sp$^2$CH(arom) at about 3050 cm$^{-1}$. Both the samples contain different hydrogen configurations and $\pi$-electrons, which is in agreement with the observation of Ohldag et al.$^7$ and Esquinazi and Hohne$^{16}$. Presence of a strong band at about 1700 cm$^{-1}$ (assigned as carbonyl group in Table 4) suggests certain polar groups are attached to the periphery of carbon network. This explains presence of oxygen in the materials under study.

Conclusions

We frankly admit presence of iron in these carbon samples. But we cannot agree with the fact that entire ferromagnetic signal resulted from the impurity, since the amount of iron detected cannot account for saturation magnetization we have observed in these carbon samples.

Secondly, following behaviours of these materials could not be explained, if we accept some ferro/ferri magnetic contaminants alone gave rise to entire ferromagnetic signals:

(i) Saturation magnetizations in both the samples are almost independent of temperature in the range of 10-300 K. This behaviour is in clear contrast to commonly known ferro/ferromagnetic contaminants, when Fe is present in such a high concentration.

(ii) The magnetization in each carbon sample increases so slowly as the temperature is lowered that no commonly known ferri/ferromagnets are known to behave similarly.

(iii) Below Curie temperature these materials do not strictly obey Curie-Weiss Law. This is also novel for any commonly known ferri/ferromagnets.

(iv) Coercivity of these carbon samples are so small that we doubted presence single domain magnetic materials, which might giving rise to such a low coercivity ferromagnetic signals. Therefore, several selected area electron diffraction diagrams were recorded randomly. But there is absolutely no evidence of presence of such contaminants.

FTIR spectra depict presence of $\pi$-electrons in these samples. It also depicts that several hydrogen configurations are attached to the periphery of carbon network in these carbon samples, which strongly corroborate others view$^{7,16}$ that the presence of spin polarized pi-electron and hydrogen may give rise to ferromagnetism in these carbon samples.

These materials may find potential application in the magnetic recording devices.

Acknowledgement

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