A Stable Carbon-based Organic Magnet

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The amorphous-like carbon compound prepared by direct pyrolysis of 1,2-diaminopropane is found to be a stable strong magnet, the apparent saturation magnetization (M_s) of which is 10.5 emu g^{-1} (0.022 μ_B per carbon atom), being comparable to *ca.* one-third of magnetite (Fe_3O_4, 30.7 emu g^{-1}).

Recently, there has been a growing interest in non-metallic organic polymer-based magnetic materials exhibiting a spontaneous magnetization at room temperature.[1-3] However, although all these compounds were air-stable at room temperature there still remained two major problems; first, the M_s value was very small and secondly, the reproducibility of the data on the magnetic behaviour was invariably poor; there were wide variations between apparently similar runs in the chemical analysis and physical properties of these materials. In the course of our work on the direct pyrolysis of organic monomers, it has been recently found that the M_s values of the carbon obtained are dependent on the ratio of hydrogen to carbon in the starting materials.[4] Thus, we have extended our research[3,4] to the use of aliphatic amines having a high H/C ratio. We discovered that 1,2-diaminopropane (H/C = 3.3) is an excellent precursor to a strong carbon magnet and, in addition, the reproducibility of the data is extremely good.

The commercially available 1,2-diaminopropane, cooled to liquid nitrogen temperature, was placed in a quartz tube, which was subsequently evacuated overnight. The tube was then heated at 950 °C and the amine, warmed to room temperature, was rapidly introduced to the heating area and pyrolysed. The reaction time was 30 min. The tube was cooled

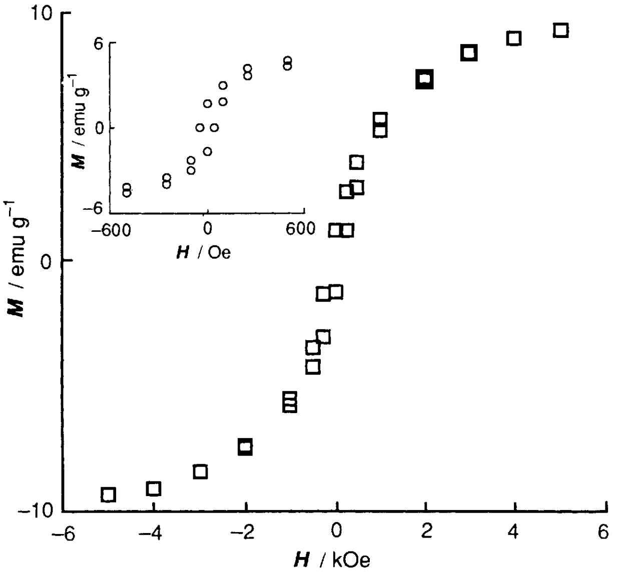

Fig. 1 Field dependence of magnetization of the carbonaceous material at room temperature. Inset: expansion of the 500 to −500 Oe region of the magnetization plot. 1 emu = 10^3 A m^{-1}.

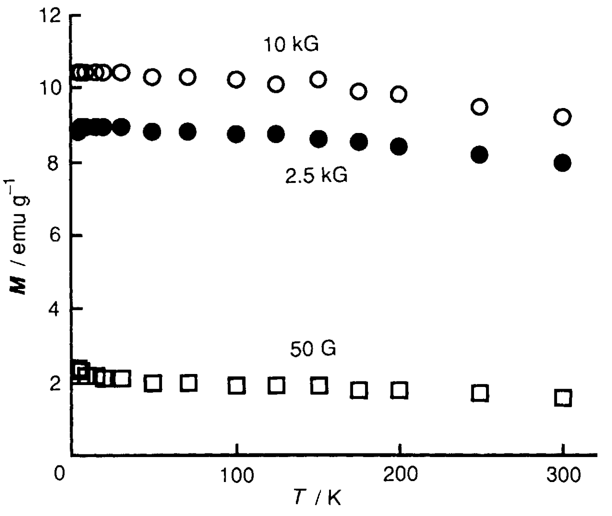

Fig. 2 Temperature dependence of magnetization of the carbonaceous material at 10.0 (○), 2.5 (●) and 0.05 (□) kG

and the resulting carbon product was removed. The carbon product obtained,† which is an insoluble but air-stable material, is amorphous-like, as shown by powder X-ray diffraction, transmission electron microscopy and electron diffraction analyses. Almost all the carbon produced was readily attracted at room temperature to a permanent magnet as weak as 200 G.

Good reproducibility in both the magnetic and ESR measurements of the carbon was observed. The field-dependence of the magnetization (*M*) of the carbon, recorded on a vibrating sample magnetometer (VSM), exhibited a clear hysteresis with a coercive force of 43 G at room temperature (Fig. 1). The saturation magnetization (M_s) was found to be *ca.* 9.2 emu g^{-1},‡ *ca.* 4–20 times those of carbon magnets previously reported[2–4] and *ca.* 3–4 times that of the vanadium–tetracyanoethylene (tcne) system (*ca.* 2.8 emu g^{-1}).[5] The temperature dependence of the magnetization, measured using a SQUID magnetometer, shows non-Curie–Weiss behaviour (Fig. 2). The M_s value slightly increases with decreasing temperature and reaches 10.5 emu g^{-1} at 4.3 K (0.022 μ_B per carbon atom): the observed M_s value corresponds to *ca.* 2.1% of the value expected by assuming that each carbon atom of the sample has a spin of a ferromagnetic unpaired electron. A remnant magnetization within a magnetic field of 50 G (Fig. 2, □) is still retained even at 300 K. The magnetic material is very stable even in air and the critical temperature§ can be >500 K, although there is some uncertainty in the determination of this value because of the decomposition of the carbon sample. The ESR spectra of the sample exhibited a relatively sharp signal [g = 2.0019 and ΔH_{PP} = 8.8 G (1 G = 1 × 10^{-4} T) at 295 K and g = 1.9724 and ΔH_{PP} = 11.3 G at 77 K] with a broad, poorly resolved signal over the range from 1000 to 6000 G; decreasing temperature results in a decrease in the broad signal intensity.

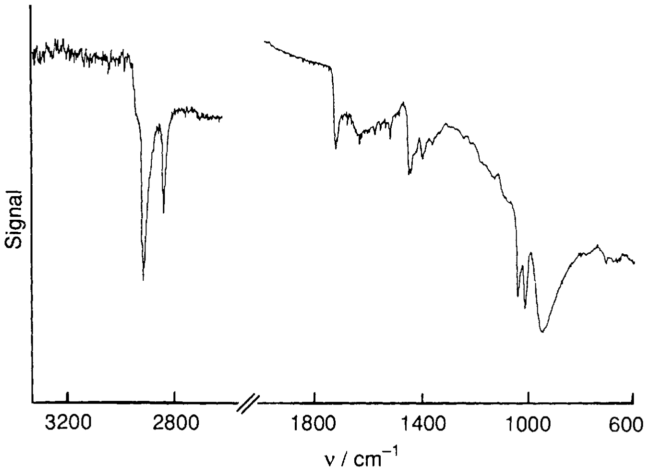

Fig. 3 The FTIR ATR absorptions of the carbonaceous film in the 600 to 3200 cm^{-1} region

We find that FTIR ATR measurements shed some light on the carbon structure, which could consist of a mixture of sp^3- and sp^2-carbons. The FTIR ATR spectra of a carbonaceous film, deposited on the quartz substrate using the diamine, exhibited integrated bands at 2850–3000 cm^{-1} and a number of bands from 1350–1750 cm^{-1}, and the bands at 850–1100 cm^{-1} (Fig. 3). The *trans*-polyacetylene has absorptions at 3012 cm^{-1} (C–H stretch of =C–H), 1910 to 1720, 1012, 892 cm^{-1} (C–H out-of-plane bend) and 1082 cm^{-1} (C–H in-plane bend).[6] Also, for partly hydrogenated *trans*-polyacetylene, there are observed the decrease in the intensities of bands at 3012, 1910 to 1720 cm^{-1} and the appearance of the bands at 2925, 2853 cm^{-1} [C–H stretch of $(CH_2)_k$], at 1464, 1452, 1442, 1432 cm^{-1} [isolated $(CH_2)_k$ bend] and at 968 cm^{-1} (C–H out-of-plane bend of isolated =C–H).[7] The C–H stretch bands of =C–H are 3040–3000 cm^{-1}, 3030 cm^{-1} for poly(phenylacetylene)s (PPA),[8] poly(1,4-phenylene) (PP),[9] respectively, while that of methyl group of methylated poly(1,4-phenylene) (MPP)[10] is 2920 cm^{-1}. Also, the C–H in-plane or out-of-plane bend bands of =C–H are 1070, 1027, 910, 870, 840, 755, 693 cm^{-1} and 1000, 800 cm^{-1} for PPA and PP, whereas, for MPP, those bands of the methyl group and =C–H are 1370 cm^{-1} and 860, 810 cm^{-1}, respectively. Taking into account the IR absorptions of these polymers previously reported,[11] these would be associated with the combined absorptions of C–H stretches and C–H in-plane and out-of-

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† From elemental analysis, nitrogen (3.01 wt%) was detected with carbon and hydrogen.

‡ Other amines such as n-propylamine, triethylamine, diethylamine, n-butylamine were found to be less effective. The synthesis of carbonaceous material from ethylenediamine (H/C = 4) was unsuccessful because of an extremely low yield.

§ The magnetization of the carbon was examined using VSM under vacuum in the temperature range between 300 and 700 K at a rate of 10 K min^{-1}.

plane bends of sp^3-carbons (–CH_2–) and/or of sp^2-carbons (=CH–). It looks likely that the formation of the sp^3-carbons could be accelerated by an atomic hydrogen generated *in situ* from the diamine under our experimental conditions.[4,12] The presence of sp^2-carbon is supported by both a high electrical conductivity (*ca.* 320 S cm^{-1}) and scanning tunnelling microscope measurements[13] of the carbonaceous film. Thus, possibly, the origin of a high M_s value and a high stability of the amorphous-like carbon obtained here is likely owing to a three-dimensional network structure consisting of both sp^3- and sp^2-carbons. Considering that the M_s value is comparable to *ca.* one-third of a ferrimagnetic magnetite (Fe_3O_4, 30.7 emu g^{-1}),[14] there might be a possibility of ferrimagnetism due to antiferromagnetic coupling between carbon high spin microregions.[15] Other likely possibilities are a superparamagnetism, since a remnant magnetization (M_r) is small relative to the M_s value (Fig. 2), although a coercive force value might not be zero and the temperature dependence of the M_s value is small.[16] Further work is underway to elucidate the observed magnetic nature.

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