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Room-temperature ferromagnetism in hydrothermally treated glassy carbon

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ABSTRACT

Extraordinary room-temperature ferromagnetism was observed in our hydrothermally treated glassy carbon systems, taken to comprise nearly graphitized regions. Strong correlation between the ferromagnetic response and the diamagnetic susceptibility, superposed together, suggests the ferromagnetic long-range order in the graphitic phase to be of itinerant nature. Besides, the graphitization process associated with the itinerant spins and the ferromagnetic order revealed a systematic correlation with the average graphitic cluster size.

1. Introduction

Ferromagnetism in carbon materials such as fullerene, graphite, carbon nanofoam, nanodiamonds, graphene, carbon nanotubes, and amorphous carbon has recently attracted considerable interest [1–10]. In particular, glassy carbon exposed to high pressures and high temperatures has shown magnetic transitions appearing along with the graphitization process [11]. In the last decade, the ferromagnetism in graphite has been intensively studied [3,4,12–14] and the ferromagnetism in fullerene has been in a controversy [15–17], while little attention has been paid on the ferromagnetism in glassy carbon. Magnetic moments in carbon have been suggested to arise from the edge states [18] and various defects [19], among which defect hydrogen may play a main role in the magnetic order [13,19]. The interaction resulting in the ferromagnetism in carbon was suggested to be the direct exchange interaction between the magnetic moments [4]. The ferromagnetic long range order also requires a lattice [14], as can be seen in the fact that amorphous carbon is not ferromagnetic but paramagnetic [11,20]. In the face-centered cubic C_{60}, the density functional theory calculations predicted the ferromagnetic long range order essentially of itinerant nature [19]. The ferromagnetic long-range order in a low-dimensional lattice such as graphene nanoribbons is an interesting question, while a two-dimensional magnetic order was suggested in graphite [21,22]. While the structural details are still controversial [23,24], the μm-size spheres characteristic of glassy carbon comprise graphitic nanostructures usually taken to be graphitic nanoribbons [23]. In this regard, ferromagnetism observed only in nearly graphitized glassy carbon deserves much attention [11].

The average in-plane size L_a of the graphitic sp^2 clusters (L_a) was reported to be smaller than ~2 nm in the amorphous carbon and to be larger than ~2 nm in the nanocrystalline graphite [25]. L_a is about 3 nm in glassy carbon [26], supporting the graphitic nanostructures as ingredients for glassy carbon, which can be taken to be intermediate between the graphitic and the amorphous states. While diamagnetism only was observed in the graphitic microparticles and paramagnetism only was observed in the amorphous phase [11], the ferromagnetism in glassy carbon may have to do with the graphitic nanoparticles. In this work, we have carried out hydrothermal treatment on the glassy carbon, which gave rise to an extraordinary room-temperature ferromagnetism. The ferromagnetic moments created by the hydrothermal treatment appear to be dictated by the graphitization process involving change in the average graphic cluster size L_a.

2. Experimental

Glassy carbon purchased from Sigma Aldrich Co. (99%) was in the form of powder of spherical particles with sizes ranging from 2 to 12 μm. Hydrothermal treatment of glassy carbon was performed at 453 K by using a 0.1-L autoclave, with 0.5 g of glassy carbon

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powder and 20 mL of ethanol, for 1, 3, 5, or 7 days, the resultant samples being denoted as “1D”, “3D”, “5D” and “7D”, respectively. The X-ray fluorescence spectroscopy (XRF) measurements on all the samples by using a Rigaku RIX 2100 showed that metal impurities such as Fe are less than the detection limit of 0.0001 wt.%. The morphology of the glassy carbon samples was examined by scanning electron microscopy (SEM), according to which the spherical particles of the glassy carbon were conserved after the hydrothermal treatments. The structures of the samples were examined by the X-ray diffraction (XRD) by using an X′pert PRO MRD diffractometer with 3-kW monochromatic Cu radiation ($\lambda = 0.154056$ nm). The Raman spectra were taken by using a lab-Ram HR with a 514.532-nm Ar laser, and the magnetization measurements were made with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS Series).

3. Results and discussion

The XRD patterns in Fig. 1(a) show broad reflections the positions of which are compatible with the hexagonal graphite [27], little difference among the patterns being observed possibly except for that in the sharp peak intensity on top of the broad (002) peak [Fig. 1(a)]. On the other hand, noticeable changes in the relative intensities of the *G* and *D* peaks of the Raman spectra, respectively representing the graphitic and the disorder phases, took place after the hydrothermal treatments [Fig. 1(b)] [25].

The average graphitic cluster size may be estimated by using the ratio of the *D* to *G* peak areal intensities obtained from fitting of the Raman spectra [Fig. 2(a)] according to [25],

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}, \tag{1}$$

for which the laser wavelength-dependent constant $C(\lambda) = 4.4$ nm was used. The L_a thus obtained is shown in Fig. 2(b) as a function of the hydrothermal treatment time.

Fig. 3(a) shows the magnetization taken at 5 K as a function of the magnetic field applied for the glassy carbon samples. In contrast to the virgin sample showing only a linear diamagnetic response,

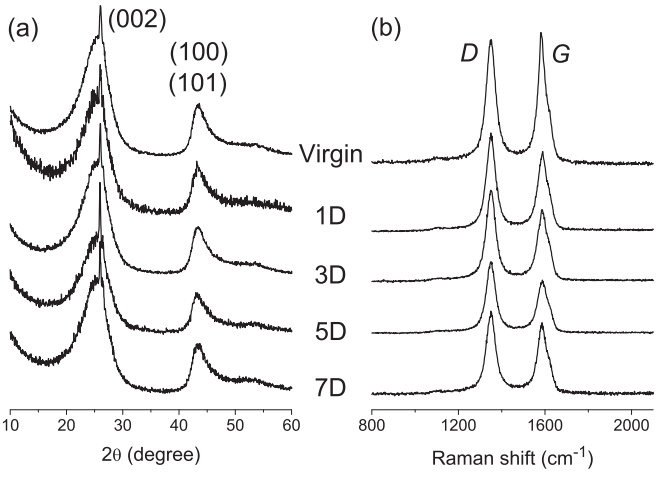

Fig. 1. (a) XRD patterns at room temperature of the glassy carbon samples, showing broad reflections whose positions are compatible with the hexagonal graphite (PDF No. 41-1487). (b) Raman spectra at room temperature of the virgin and hydrothermally treated glassy carbon samples showing pronounced *D* and *G* peaks at 1350 and 1584 cm^{-1}, respectively. The *D′* peak arises from the very small size of the sp^2 domains in the glassy carbon.

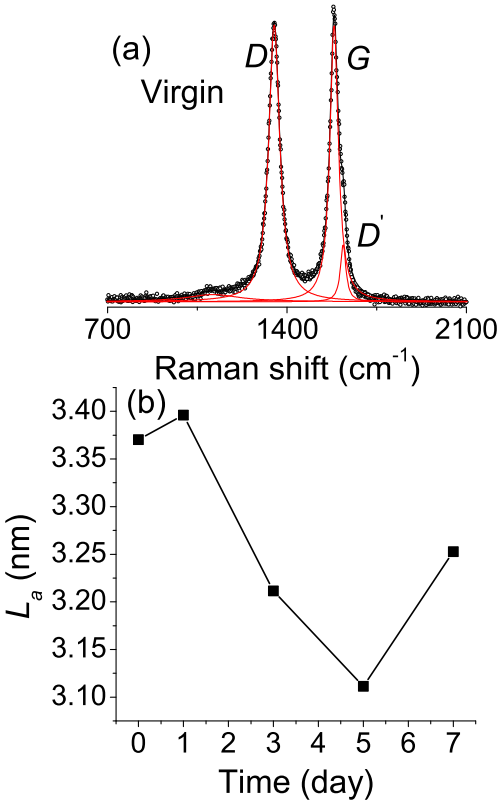

Fig. 2. (a) Raman spectrum of the virgin glassy carbon, fitted by the Lorentzian components with the *G* peak at 1584 cm^{-1}, *D* peak at 1350 cm^{-1}, and the *D′* peak at 1619 cm^{-1} arising from the very small size of the sp^2 domains in the glassy carbon. (b) The in-plane size of the sp^2 graphitic clusters (L_a) as a function of the hydrothermal treatment time.

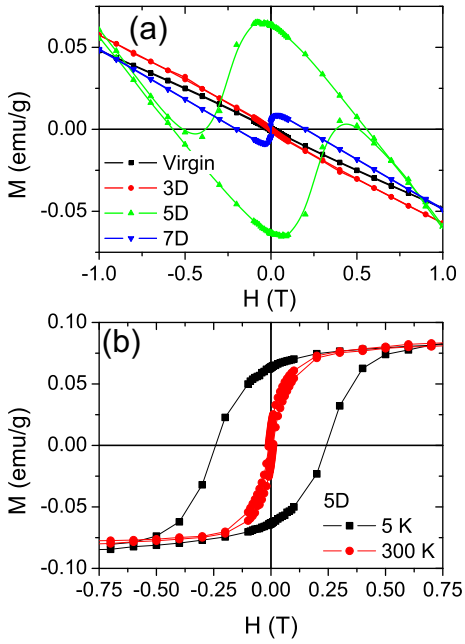

Fig. 3. (a) Magnetization vs the magnetic field (*M–H*) measured at 5 K, exhibiting ferromagnetic hysteresis in the hydrothermally treated samples. (b) Magnetic hysteresis loops of the 5D sample measured at 5 K and 300 K after subtracting the linear diamagnetic contributions.