



## Room temperature ferromagnetism in naphthalene

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### ABSTRACT

Exploration of high temperature organic magnets is one attractive topic in the fields of physics, chemistry, and material science. Here, we show that by using a two-step method - ultrasound treatment and low temperature annealing, room temperature ferromagnetism can be produced in naphthalene, the simplest polycyclic aromatic hydrocarbon consisted of two fused benzene rings. The existence of hydrogen after processing naphthalene suggests that the observed ferromagnetism can be attributed to carbon dangling bonds on naphthalene molecules. This is supported by theoretical simulations showing that two separated dangling bonds prefer the ferromagnetic ordering. Our finding opens a window for the systematic search of new high temperature organic magnets in the large family of hydrocarbons.

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### 1. Introduction

Ferromagnetism (FM) in carbon-based materials has been attracting great attention due to its potential application prospect and fundamental importance for understanding the ferromagnetic mechanism of s and p electrons. Recently, room temperature FM has been observed in several carbon nanostructures, including highly oriented pyrolytic graphite [1–5], polymerized fullerenes [6], carbon nanotube [7], and nitrogen- and carbon-ion-implanted nanodiamond [8]. Hydrogen was shown to play an important role in triggering FM in graphite and carbon nanotube [4,5,7]. Besides, the observation of room-temperature magnetic order in hydrogenated epitaxial graphene [9] and on zigzag edges of narrow graphene nanoribbons [10,11] raises hopes of operating graphene-based spintronic devices at ambient conditions. Theoretical calculations indicated that intrinsic defects, such as carbon dangling bonds or vacancy-interstitial complexes, are responsible for the magnetism of carbon nanostructures [12–14].

Significant progresses have also been made for molecule/

organic polymer-based magnets [15–19]. For instance, coexistence of FM and metallic conductivity was realized in bis(ethylenedithio)tetrathiafulvalene-based layer compound [15]. Room temperature FM was observed in the reaction products of bis(1,5-cyclooctadiene)nickel with the organic oxidizing agents tetracyanoethylene, 7,7,8,8-tetracyanoquinodimethane, or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [16]. In Teflon and polyethylene, room temperature FM was observed through very simple methods - cutting or mechanical stretching [19]. First principles calculations indicated that FM is originated from carbon dangling bonds and strong ferromagnetic coupling between them [19].

Inspired by dangling bonds induced FM in carbon nanostructures and polymers, we develop a two-step method - ultrasound treatment and low temperature annealing to explore FM in the molecule-based organic materials. We start from the simplest polycyclic aromatic hydrocarbon - naphthalene, which has been widely used in industry for producing phthalic anhydride and azo dyes [20,21]. The magnetic measurements showed that room temperature FM is realized in the processed naphthalene. The existence of hydrogen after processing naphthalene suggests that the observed ferromagnetism can be attributed to carbon dangling bonds on naphthalene molecules. This is supported by theoretical simulations showing that two separated dangling bonds prefer the ferromagnetic ordering. Our finding illustrates a new route for the search of high temperature organic magnets in the organic hydrocarbons.

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## 2. Experiments

### 2.1. Material synthesis

Naphthalene (purity:  $\geq 99.5\%$ ) with weight of 0.2 g was loaded into a quartz tube with a diameter of 10 mm and sealed under a vacuum about  $1 \times 10^{-4}$  Pa. After treating the sample tubes in an ultrasound device at 80 °C for 10 h, they were heated at 130–170 °C for one day.

### 2.2. Material characterization

Purchased naphthalene was analyzed by using inductively coupled plasma atomic emission spectrometry (ICP-AES). It was put into nitric acid ( $\text{HNO}_3$ ) or hydrofluoric acid and sealed in Teflon container. After ultrasound treatment for half hour to make sure all existed metal ions will solve in the solvent, the solution in the container was then measured by ICP-AES. The measured results showed that no characteristic peaks for Fe/Co/Ni appear in the atomic emission spectra. This indicates that if there is any magnetic impurity, its concentration should be less than the detecting limit of 0.05 ppm. The same ICP-AES detecting procedure was also applied for annealed naphthalene, and no characteristic peaks for Fe/Co/Ni were detected, suggesting that no magnetic impurity is introduced in the process of synthesis.

The annealed samples were placed into nonmagnetic capsules for characterization in an argon-filled glove box with both of  $\text{H}_2\text{O}$  and  $\text{O}_2$  concentrations less than 0.1 ppm. Magnetization measurements were performed with a SQUID magnetometer (Quantum Design MPMS3) in the temperature range of 1.8–300 K. Before each measurement, we performed the oscillatory demagnetization and magnet rest (heating magnet) to ensure the accuracy of magnetic field. The crystal structures of pristine and potassium-doped materials were measured on a D8-Advance X-ray diffractometer. The Raman scattering spectra were collected at room temperature on an in-house system with Charge Coupled Device and Spectrometer from Princeton Instruments in a wavelength of 660 nm and power less than 1 mW. The gas inside the quartz tube was examined by gas chromatograph (GC-2018, Shimadzu, Japan, TCD, 5 Å molecular sieve column).

### 2.3. Theoretical calculations

Our theoretical calculations were performed by using the plane-wave pseudopotential method as implemented in the Vienna *ab initio* simulation package (VASP) program [22,23]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formula [24] for the exchange–correlation potentials and the projector-augmented wave method (PAW) [25] for ionic potential were used to model the electron–electron and electron–ion interactions. Considering the non-local interaction, we have included the correction of van der Waals (vdW) in the version of vdW-DF2 [26]. For the plane-wave basis-set expansion, an energy cutoff of 600 eV was adopted. The Monkhorst–Pack *k*-point grids were generated according to the specified *k*-point separation of  $0.02 \text{ \AA}^{-1}$  and the convergence thresholds were set as  $10^{-6}$  eV in energy and  $10^{-3}$  eV/Å in force. To simulate the (001) surface, a supercell slab model [27,28] was used, with two naphthalene layers separated by a 15 Å vacuum region, which ensures that there is negligible interaction between surfaces in neighboring cells. The carbon dangling bonds were built by removing H atoms exposed on the slab surface.

## 3. Results and discussion

Pristine naphthalene exhibits the diamagnetic behavior, which

is clearly characterized by the opposite signs of magnetization and magnetic field as shown in Fig. 1b. Fig. 1a shows the temperature dependence of  $\chi$  for one sample annealed at 130 °C (labeled as N14) in the temperature range from 1.8 K to 300 K under various magnetic fields. One can readily see that the field cooling (FC) and zero-field cooling (ZFC) curves do not merge up to 300 K when applying low magnetic fields for the annealed sample. This indicates the existence of magnetic ordering with a critical temperature ( $T_c$ ) above room temperature. As the magnetic field increases to 2000 Oe, the disparity between the two curves disappears, reflecting the saturation of magnetization. To understand the magnetic property of sample N14, the corresponding *M*–*H* loops measured at 1.8 K and 300 K are shown in Fig. 1b. The magnetic hysteresis clearly appears at 1.8 K and 300 K, indicating that the FM phase already forms at room temperature. The saturation magnetization is reduced only 4.4% when temperature is increased from 1.8 K to 300 K, and the coercivity is reduced from 215 Oe to 156 Oe. Similar magnetic hysteresis loops were also observed in other samples, and the representative results for two samples annealed at 170 °C (labeled as N27 and N31) are presented in Fig. 2.

To examine the stability of FM and eliminate the possibility of unintended magnetic impurity, the sample powder of N14 in the capsule with total weight of 10.3 mg was divided into two parts one month after the initial measurement. One part with weight about 6.3 mg was resealed immediately in the capsule for magnetization measurement, and the other part with weight about 4.0 mg was exposed in glove box at room temperature for 1 h and then resealed for magnetization measurement. The corresponding *M*–*H* loops for the two parts are shown in Fig. 1c and d, respectively. It is found that the *M*–*H* loops in Fig. 1c are very similar to the ones in Fig. 1b, demonstrating that FM is stable and uniformly distributed in the sample. On the other hand, the *M*–*H* loops become flattened for the 4.0 mg sample after being exposed in glove box for 1 h, implying a substantial destruction of FM. Here, a linear diamagnetic background was subtracted for the 4.0 mg sample. The change of *M*–*H* loops indicates that the observed FM is sensitive to the environment, and therefore, uniformly distributed magnetic impurities can be safely excluded in our experiments.

A comparison of the crystal structures and chemical bonding before and after annealing was made to understand the intrinsic origination of FM. Fig. 3a presents the Raman spectra of samples N14, N27, N31, and pristine naphthalene. The peak positions for the pristine material are in good agreement with the ones in the literatures [29,30]. No Raman shift can be observed after annealing, indicating that the newly recrystallized naphthalene has the same molecular structure as the purchased one. The corresponding X-ray diffraction (XRD) patterns are compared in Fig. 3b. It is clearly seen that the purchased naphthalene has a preferred orientation growth along the [001] direction, and the strongest peak (111) in the PDF card (C10H8#13–0824) almost vanishes. Upon vacuum annealing, the preferred orientation growth is greatly suppressed, evidenced by the appearance of the strongest peak (111). One can notice that the intensity ratio for the (001) and (111) peaks is reduced according to the sample order N31, N27, and N14, accompanying a strong increase of the corresponding saturated magnetization (see Figs. 1 and 2). This clearly indicates that more exposed (001) planes induced by stronger suppression of the preferred [001] growth benefit the formation of FM. The XRD results suggest that FM is related to a certain factor that affects the recrystallization of naphthalene.

One highly possible reason for suppressing the preferred [001] orientation growth is the formation of carbon dangling bonds on the naphthalene (001) surface, which can simultaneously produce magnetic ordering [19]. To verify this hypothesis, a comparison experiment was performed for two samples (labeled as C1 and C2)

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