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Observation of ferromagnetism in black phosphorus nanosheets with high magnetization by liquid exfoliation

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ABSTRACT

The Black Phosphorus (BP) nanosheets were prepared by liquid ultrasonic exfoliating the grinded layered BP bulk in organic solutions under protecting atmosphere. The samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), as well as selective electron diffraction (SED). The possible magnetic (Fe, Co, Ni) impurities in the BP material were analyzed by an inductively coupled plasma-atomic emission spectrometry (ICP-AES). Magnetization measurements were performed using a vibrating sample magnetometer (VSM, Quantum Design PPMS-9T). The results indicate that the BP nanosheets sample has a weak ferromagnetic ordering with high magnetization 1.83 emu/g at room temperature. Analysis states the ferromagnetism is intrinsic to the BP samples, ruling out extrinsic ferromagnetism arising from magnetic metal impurities. The combination effects of magnetic moments resulting from defects or vacancies, the formation of edge states and the p orbital spin polarization of the oxygen and phosphorus atoms of the surface P—O bonds contribute to the observed ferromagnetism in BP nanosheets sample. The conversion of ferromagnetism of 2D material BP at room temperature will be of great implication for spintronics application in the future.

1. Introduction

Black phosphorus (Phosphorene) has attracted great interests owing to its novel electronic structures and optoelectronic properties [1–3]. For instance, high carrier mobility of 1000 cm^2/V s [4–8], large on-off ratio of 10^5 [4], thickness-dependent direct band gaps ranging from about 2.0 eV for a monolayer to about 0.3 eV for the bulk [4–6,9], novel quantum effects [10–13], tunable semiconductor-to-metal transition and optoelectronic properties controlled by strain, doping or edge defects [14–19], fast photo-response [20–26], and so forth. Besides these unique properties which are currently at the forefront of research focus, the magnetism of phosphorene also draws extensive attentions [27–52]. It is well known that if magnetic moment can be introduced into phosphorene, the applications of phosphorene will be extended more widely in nanoelectronics and spintronics. Numerous theoretical works have intensively investigated the spin polarization properties of modified phosphorene.

Perfect black phosphorus (Phosphorene) crystal itself has no magnetic moment. The first principle calculation shows that one can produce ferromagnetism or antiferromagnetism in black phosphorus (Phosphorene) crystals through the formation of vacancies and defects [27–30], adsorption of nonmetal atoms or metal atoms [31–35], doping transition metal atoms or nonmetal atoms [35–44], nanoribbons [45–49], strain [27,28,35,40,48], O-saturated [45,46], external electric field [50–52], and so on.

However, there are only a few studies devoted to the experimental work on the magnetic properties of BP (Phosphorene). An extreme anisotropy of the magnetic properties, i.e. diamagnetic/paramagnetic behavior with a magnetic field perpendicular to the basal/edge plane was detected for BP crystal [53]. Tunable weak d^0 ferromagnetism was demonstrated in BP crystal by electrochemical oxidation [54]. Large room-temperature edge ferromagnetism (FM) obtained from oxygen (O)-terminated zigzag pore edges of few-layer BP nanomeshes was experimentally evidenced [55]. In this paper, we prepared large quantities of BP nanosheets by liquid phase exfoliation [56–58] and studied the magnetic properties of then by vibrating sample magnetometer (VSM) integrated into a physical property measurement system (PPMS-9T, Quantum Design).

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2. Experiments

In the present work, the layered BP crystal was synthesized by the improved vapor transport method as described in details in references [59–61]. The ultra-thin BP nanosheets were prepared by ultrasonic exfoliating the grinded layered BP bulk in organic solutions (anhydrous alcohol) under protecting atmosphere (N2). The BP suspension was dropped onto a clean Si substrate for scanning electron microscopy (SEM) characterization and Raman measurement, and onto an ultrathin carbon-coated holey carbon support film with 300 mesh copper grid for TEM characterization. The phase composition of BP crystal powders was analyzed by X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku Smartlab3) with Cu Ka radiation (λ = 1.5406). Raman spectroscopy of PB bulk and nanosheets were performed using a Horiba Jobin Yvon LabRAM HR-800 Raman microscope (λ = 514 nm, power = 1 mW, beam spot = 1 μm) at room temperature and under ambient conditions. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALab250Xi K-alpha XPS spectrometer for the ultrasonic exfoliated BP sample. The base pressure was about 3×10^{-9} mbar. The binding energies were corrected to the C1s line at 2848 eV from adventitious carbon. The morphologies of the samples were investigated by Phenom ProX desktop scanning electron microscopy (SEM) and transmission electron microscopy (TEM, FEI Tecnai F20). The magnetic properties of the samples (bulk BP, grinded BP, ultrasonic exfoliated BP and centrifugal BP nanosheets) were performed using a VSM integrated in a PPMS-9T with the accuracy of 10^{-7}emu. The ferromagnetic behavior was confirmed by isothermal magnetization versus applied magnetic field (M-H) measurements. Raw measurements of the magnetization vs. applied magnetic field were corrected for the diamagnetic contributions from the substrate and the BP crystal by subtracting the linear response measured at high fields. The mount of possible magnetic impurities (Fe, Co, Ni) in the BP material was measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian Vista MPX) with a resolution < 0.004 nm and a detection limit in PPB-PPM grade.

3. Results and discussion

To better investigate the crystalline of BP sample, we utilize the XRD analysis. Fig. 1 (a) shows the XRD pattern for the as-synthesized BP powders. All the diffraction peaks in the XRD pattern can be readily indexed to the orthorhombic Cmca phase structure (a = 3.313, b = 10.473, c = 4.374, α = β = γ = 90) [60,61]. Typical Raman spectrum of as-grown BP bulk, grinded BP and BP nanosheets with three major bands are shown in Fig. 1(b). The observed modes A_g^1 (one out-of-plane vibration mode), B_{2g} and A_g^2 (two in-plane vibration modes) of BP bulk and grinded BP can be easily detected at wave numbers of 361.5 cm^{-1},438.4 cm^{-1}, and 466.2 cm^{-1}, respectively, which is in good agreement with previously reported results [58–60]. The peak positions are consistent with the signature Raman spectrum of the mechanically exfoliated BP flakes, suggesting that the flakes are crystalline after the ultrasonic exfoliation. The three Raman peaks of BP nanosheets (phosphorene) are 356.5 cm^{-1},430.4 cm^{-1}, and 457.5 cm^{-1}, respectively. It is likewise shown that the red shift of the Raman peaks of phosphorene [62].

Fig. 1(c) shows that XPS of the as-prepared BP flakes with the $2p^{3/2}$ and $2p^{1/2}$ doublet at 129.9 and 130.8 eV, respectively, which characterize the crystalline of BP. Oxidized phosphorus (i.e., POx) subbands are also apparent at ~134.1 eV, which likely stems from oxygen defects or surface suboxides in the BP. The suboxides are also observed in previous measurement samples exfoliated in a solvent [58–60]. It has been reported that BP is sensitive to water and oxygen and can be degraded to PxOy under visible light irradiation [58–60]. Therefore, the O signal should arise from the oxidation of BP, owing to the exposure of BP samples to the atmosphere before XPS measurement.

To better understand the character of the BP sample, scanning

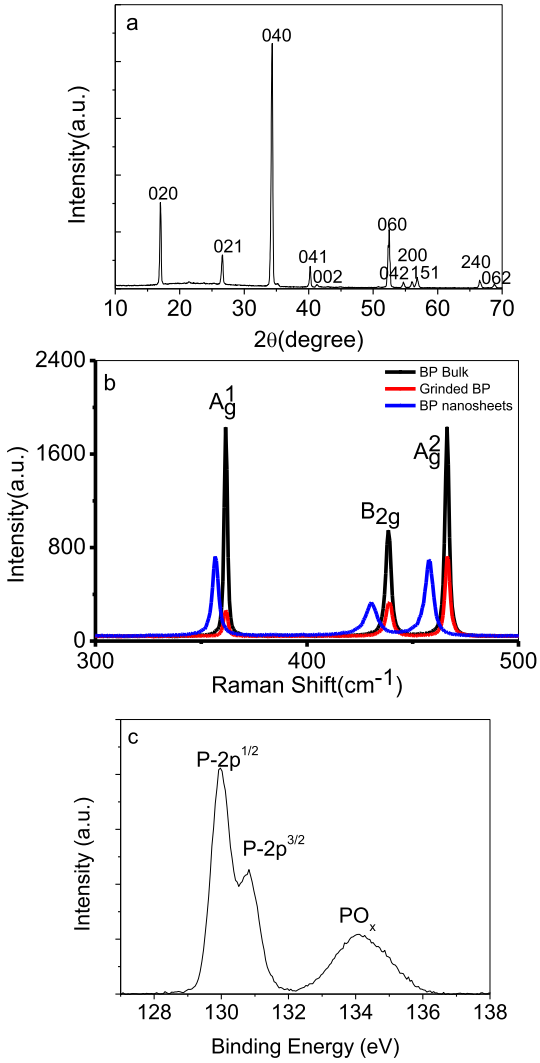

Fig. 1. (a) X-ray diffraction (XRD) data of bulk BP crystal. (b) Raman spectrum of BP bulk (black) Grinded BP (red, the peaks of A1 g, B_{2g}, and A2 g are 361.5 cm^{-1}, 438.4 cm^{-1}, 466.2 cm^{-1} respectively) and BP nanasheets (blue, the peaks of A1 g, B_{2g}, and A2 g are 356.5 cm^{-1}, 430.4 cm^{-1}, 457.5 cm^{-1} respectively). (c) X-ray photoelectron spectra (XPS) of liquid exfoliated BP. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

electron microscopy (SEM) measurement was studied. Fig. 2 (a, b) present the typical scanning electron microscopy (SEM) surface images of BP bulk and ultrasonic exfoliated BP sample. The typical layer structure is obvious in Fig. 2 (a), and large quantities of irregular edges can be found from the images of Fig. 2 (b). Fig. 2 (c) displays the typical transmission electron microscopy (TEM) image of BP nanosheets on a copper grid with carbon support. The high-resolution lattice image Fig. 2 (d, e) and the selective diffraction patterns Fig. 2 (f, g) indicate that the BP nanosheets are highly crystalline.

In order to understand the magnetic character of the BP sample, PPMS measurement was investigated. Fig. 3 presents the typical M-T curve of the BP nanosheets measured from 5 to 300 K under the applied field H = 1000 Oe. The curve indicates a ferromagnetic ordering Tc of the sample above 300 K. Fig. 4 shows the mass magnetization (M-H) curves of BP bulk, grind BP, ultrasonic exfoliated BP and centrifuged (3000 rpm) BP nanosheets samples at room temperature, respectively. Expecting the diamagnetic characteristic of the BP bulk sample in Fig. 4 (a), which is intrinsic to the BP crystal [53], the magnetic hysteresis (By subtracting the diamagnetic signal from the observed data, one can