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Liquid exfoliation of black phosphorus nanosheets and its application as humidity sensor

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ABSTRACT

The bulk crystal of black phosphorus was exfoliated by liquid exfoliation method for a duration of 8 h using N-Methyl-2-Pyrrolidone as the solvent. The exfoliated sample was centrifuged at different rpm such as 3000, 5000 and 10,000 to separate out the 2D black phosphorus nanosheets with different thickness and length. The as synthesized black phosphorus nanosheets collected at these rpm values were characterized with TEM, AFM, Raman spectroscopy and Vis-NIR spectroscopy. Further, we investigated the humidity sensing behaviour of the devices fabricated by using these samples. The results obtained show that the device fabricated with black phosphorus nanosheets and nanoparticles obtained by filtration of the sample collected after 10,000 rpm exhibited better performance as compared to the nanosheets collected at 3000 and 5000 rpm. The response and recovery times of devices are found to be promising and better than those of the black phosphorus gas sensor reported earlier. The present investigations open up a new avenue for further studies in improving the performance of black phosphorus nanosheets based gas sensing devices.

1. Introduction

Two dimensional semiconducting layered materials such as transition metal dichalcogenides (TMDCs) have attracted great attention since the inception of search for materials with extraordinary electrical, optical and magnetic properties suitable for nanoelectronic device applications [1–9]. The Black phosphorus is one of the monotype layered two dimensional (2D) crystals [10–12]. Black phosphorus nanosheets have been reported to exhibit a high mobility of 1000 $cm^2\ V^{-1}\ s^{-1}$ for a sample of thickness of 5 nm with high current ON/OFF ratio of 10^5 [10]. The band gap of black phosphorus was observed to be layer dependent which increases with decrease in number of layers with a value of 0.3 eV for the bulk crystal and 2.0 eV for the single layer [10–14]. This is exactly similar to TMDCs but with an additional advantage of a direct band gap from bulk to single layer, while the band gap changes from indirect to direct as the layer number is reduced from bulk to monolayer in the case of TMDCs [3–6,9,17,25]. Importantly, the bulk black phosphorus has been observed to be inherently a p-type semiconductor [15,16]. A single layer of black phosphorus consists of phosphorus atoms covalently bonded to three nearby phosphorus atoms forming puckered structure [18]. In a bulk black phosphorus each of the single layers of P atoms are bonded to their adjacent layers through van der Waal's weak forces [11–14,17,18].

For the development of nanoelectronics and photonic devices based on 2D materials they should have an ideal energy band gap in order to cover the wide range of electronic devices. [14,19,26,39,41,56]· The band gap of these materials can be tuned by 50% as the materials can be thinned down to single layers [18]. Thus, in the case of black phosphorus the layer dependent band gap values lay between those of graphene and semiconducting TMDCs [11]. As a result it covers the entire range of spectrum from 0 to 2.0 eV supported by other layered materials. The change in band gap of black phosphorus can be used in the devices which operate at IR optoelectronic to high mobility quantum transport devices [10].

Further, for black phosphorus the electron effective mass is observed to be several times lighter in armchair direction than in the zigzag direction [10,14]. On integrating the possible perspectives the layered black phosphorus can have new characteristics and extraordinary properties for anisotropic electronic, optoelectronic, mechanical or magnetic properties. Recently there have been huge studies on 2D black phosphorous materials based devices such as photodetectors, field effect transistors and other optoelectronic devices [53]. Black phosphorus either in the form of

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single layer or few layers has so far been reported as a field effect transistor, photodetector, and p–n junction diode in heterojuction with MoS_2, radio frequency transistors etc. [12–18,40,41].

The humidity sensors are among the most significant devices of importance in industry and instrumentation requirements. Monitoring and control of humidity in the industries, equipments, laboratories and in environment is of high importance and essential for safety precautions. Development of sensing devices with quick response and recovery times, ability to sense wide range of humidity with high sensitivity and stability is a frontier area of research in sensor. Among the materials studied for fabricating the humidity sensors includes the ceramics, metal oxides, nanowires, semiconductor nanoparticles, and composite heterostructure etc. [20–23] However, these low-dimensional nano-heterostructures based sensors mostly limited to operate only at high temperature. The 2D graphene nanosheets has been utilized to sense the individual gas molecules, which lead to the ultimate limit of the sensitivity [1b]. The 2D inorganic layered materials such as MoS_2 have attracted a keen interest as perspective sensor materials for next generation due to their high surface to volume ratio which can translate into extremely sensitive gas-sensor device via charge transfer on the surface and 2D planar structure favouring easy fabrication of devices.

The 2D materials have also been tested for the humidity and gas sensing performance which including graphene, reduced graphene oxide and its composites with other materials and inorganic layered materials such as MoS_2, WS_2, $MoSe_2$ etc. [24–37,58] Though, black phosphorus has many attractive properties for optoelectronic device application so far it has not been tested for its performance towards humidity sensing. Black phosphorus is expected to possess high surface area due to its puckered structure. It is known that single to few layer thick black phosphorus nanosheets are very much sensitive to moisture [13,38,50,52,59,60]. This property of black phosphorus could be taken advantage in the sensing of humidity. However, till date there are only a few theoretical articles describing black phosphorus as a perspective sensor material for ad-atoms, physisorption of molecules such as CO, H_2, H_2O, NH_3, NO, and NO_2 etc. [42–45] Recently, there is a experimental report on the $N0_2$ gas sensor based on black phosphorus nanosheets to the best of knowledge [46]. Here, in this article the humidity sensing behaviour of black phosphorus nanosheets of three different thickness ranges and lengths synthesized by the well known liquid phase exfoliation method has been demonstrated [6–8,47–49].

2. Experimental section

2.1. Materials

Bulk crystals of Black Phosphorus were purchased from smart-elements (GmbH, Ferrogasse 4/1, 1180 Vienna, AUSTRIA) and N-Methyl-2-Pyrrolidone from High Purity Laboratory Chemical Manufacturers, Mumbai, India. LiCl, $MgCl_2$, K_2CO_3, NaBr, KI, NaCl, KCl and K_2SO_4 salts were purchased from Thomas Baker Chemicals private limited (Mumbai, India) and were used as received.

2.2. Black phosphorus nanosheets and nanoparticle synthesis

Black phosphorus nanosheets and nanoparticles were synthesized by the well known liquid phase exfoliation method through simple ultrasonication in solvent. There are recently few reports on the liquid exfoliation of black phosphorus to produce few layered nanosheets [47–49]. For the liquid exfoliation we used N-methyl-2-pyrrolidone (NMP) as the solvent since NMP produces stable and concentrated dispersions as demonstrated for many layered materials such as TMDCs and graphene as well [6–8]. In this report we carry out ultrasonication of black phosphorus bulk crystal in NMP for 8 h at room temperature. At first, bulk crystal of black phosphorus was ground into powder and transferred into a glass vial with a concentration of 1 mg/ml of NMP. Followed by transferring the sample into vial, Argon gas was passed inside the vial and immediately closed and covered with paraffin film and Teflon tape. This dispersion was then subjected to ultrasonication in a bath sonicator (BRANSON ultrasonicator 3800, with a 40 kHz transducer and a power of 110 W). The temperature of the sonication bath was maintained at room temperature and during exfoliation the vial was shaken after every 1 h so that the unexfoliated crystals settled at the bottom would disperse in the solution and the exfoliation happens effectively. Followed by ultrasonication centrifuging the exfoliated product at different rpm values result in the black phosphorus nanosheets of different thickness and lateral dimension. After 8 h the exfoliated dispersion of nanosheets was centrifuged (TARSON SPINWIN Microcentrifuge MC-02) at 3000 rpm for 10 min and the supernatant was collected and further centrifuged at 5000 rpm. The supernatant obtained after 5000 rpm was again centrifuged at 10,000 rpm for 15 min and the bottom settled product is separated from the supernatant. After each step of centrifugation the precipitate was washed twice in ethanol to remove the traces of NMP that could possibly be present. Further, we dispersed this clump of nanosheets and nanoparticles obtained after 10,000 rpm in ethanol and sonicated for few minutes to make a proper dispersion of the sample. Finally this mixture was filtered using RanDisc syringe filter with a pore size of 220 nm in order to separate the nanosheets and nanoparticles.

2.3. Material characterization

The products obtained were characterized with transmission electron microscopy (TEM), Raman spectroscopy and UV–Vis–NIR absorption spectroscopy. TEM analyses were done using the instrument FEI TECNAI G2 F-20 (FEG), Raman spectroscopy was done with Horiba JY Lab Raman HR 800 Micro Raman Spectrometer equipped with a 632.8 nm laser and the UV/VIS/NIR absorption spectrum was recorded using Perkin Elmer Lambda 900 UV–Vis–NIR spectrometer. Atomic force microscopy (AFM) was carried out using the instrument Nanosurf Easyscan2. For AFM the samples were prepared by dispersing the black phosphorus nanosheets in ethanol and drop casting over cleaned Si substrates. For TEM characterization samples were prepared by drop casting the black phosphorus nanosheets/nanoparticles over a copper TEM grid coated with carbon film. For Raman characterization the samples were drop casted onto silicon substrate, and for UV–ViS–NIR absorption the samples were dispersed in ethanol.

2.4. Device fabrication

The sensor devices were fabricated in two probe geometry by drop casting the black phosphorus nanosheets onto ITO coated glass substrates with an electrode separation of ~250 μm. Black phosphorus nanosheets were dispersed in ethanol for drop casting purpose.

2.5. Humidity sensing

In order to generate the different relative humidity (RH) environments we use aqueous saturated salt solutions of LiCl, $MgCl_2$, K_2CO_3, NaBr, KI, NaCl, KCl and K_2SO_4. It is known that aqueous saturated solutions of these salt solutions generate approximate relative humidities of 11.3%, 32.8%, 43.16%, 57.57%, 68.86%, 75.29% 85.06% and 97.3% respectively [57]. Humidity sensing