SUPPORTING INFORMATION

Few-layer black phosphorus nanoparticles

Zdenek Sofer*a, Daniel Boušaa, Jan Luxaa, Vlastimil Mazaneka, and Martin Pumera*b

Synthesis

Materials

Red phosphorus (99.999%), tin (99.999%), gold (99.999%), iodine (99.9%), bis(2-methoxyethyl) ether (DIGLYM), 1-methyl-2-pyrolidone (NMP), N,N-dimethylformamide (DMF) and acetonitrile (AN) were obtained from Sigma-Aldrich, Czech Republic. Carbon disulfide was obtained from Lach-Ner, Czech Republic.

Black phosphorus synthesis

Black phosphorus crystal synthesis was based on the procedure reported in the literature using a Au/Sn alloy like solvent for red phosphorus and Snl₄ as a mineralizing agent in a sealed ampoule. 750 mg of AuSn alloy was prepared by a melting stoichiometric amount of tin and gold under high vacuum directly in the ampoule used for synthesis. 1080 mg of red phosphorus and 23 mg of Snl₄ were added to the quartz ampoule and subsequently sealed using an oxygen/hydrogen torch. The ampoule was placed in a muffle furnace and heated to 400 °C in 1 hour. After holding for 2 hours at 400 °C the ampoule was heated to 600 °C and held on this temperature for 24 hours. The furnace was then cooled to room temperature overnight. The result was crystals of black phosphorus in the form of plates with sizes of up to 15 mm x 4 mm, which were removed from ampoule and washed with CS_2 to remove white phosphorus formed as a byproduct. Vapour transport growth crystals are shown in **Figure 1**. Snl₄ was prepared by direct synthesis using iodine and tin in chloroform under reflux. Snl4 was purified by recrystallization from chloroform.

Black phosphorus exfoliation

Synthesized crystals of black phosphorus were milled using agate mortar (10 minutes) and ultrasonicated in solvent used for subsequent milling for 30 minutes (400 W, room temperature). Subsequently black phosphorus suspension in solvent was milled using Ultra Turrax disperser for different time and speed in various solvents (**see Figure S1**). To avoind overheating the milling tube was cooled with ice. The milling was performed under argon atmosphere to avoid black phosphorus oxidation. Systematic measurement of particle size dependence was performed for 16 000 rpm using dimethylformamide (DMF), 1-methyl-2-pyrolidone (NMP), bis(2-methoxyethyl) ether (DIGLYM) and acetonitrile. In addition the milling in DMF was performed using 11 000 rpm. The milling time was up to 6 hours. The sampling for characterization was performed at 0.5 hour and each following hour. In order to use the homogeneous mixture for analysis the sampling was performed during the milling. The measurement of milling yield and particle size distribution was performed on suspension after 48 hours of sedimentation. The smallest black phosphorus nanoparticles were separated from the suspension by centrifugation using 5 000 rpm and 10 000 rpm.

Characterizations

The morphology of the black phosphorus nanoparticles was investigated using scanning electron microscopy (SEM) with a FEG electron source (Tescan Lyra dual beam microscope) and STEM sample holder. To conduct

the measurements, the nanoparticles suspension was drop casted on 200 mesh Cu TEM grid and dried in vacuum oven (50°C). STEM measurements were carried out using a 30 kV electron beam.

The AFM measurements were carried out on an Ntegra Spectra from NT-MDT. The surface scans were performed in a tapping (semi-contact) mode. Cantilevers with a strain constant of 1.5 kN.m⁻¹ equipped with a standard silicon tip with a curvature radius lower than 10 nm was used for all measurements. The black phosphorus nanoparticles suspension was drop casted on the freshly cleaved mica substrate and dried in vacuum oven (50 °C).

X-ray diffraction was performed with a Bruker D8 Discoverer diffractometer in Bragg–Brentano parafocusing geometry using CuK α radiation. Diffraction patterns were collected for 2 θ values from 5° to 80°. The data obtained were evaluated using HighScore Plus 3.0e software.

An inVia Raman microscope (Renishaw, England) with a CCD detector was used for Raman spectroscopy and photoluminescence measurement in the backscattering geometry. A Nd-YAG laser (532 nm, 50 mW) with a 50× magnification objective was used for measurements. Instrument calibration was performed with a silicon reference which gives a peak centre at 520 cm⁻¹ and a resolution of less than 1 cm⁻¹. In order to avoid radiation damage, the laser power output used for this measurement was kept below 5 mW. The black phosphorus nanoparticles suspension was drop casted on the silicon substrate and dried in vacuum oven (50 °C).

High resolution X-ray photoelectron spectroscopy (XPS) was performed using an ESCAProbeP (Omicron Nanotechnology Ltd, Germany) spectrometer equipped with a monochromatic aluminium X-ray radiation source (1486.7 eV). A wide-scan survey with subsequent high-resolution scans of the P 2p core level was performed. Relative sensitivity factors were used in the evaluation of composition from the survey spectra. The black phosphorus quantum dots suspension was drop casted on the freshly evaporated gold on silicon substrate and dried in vacuum oven (50 °C).

The dynamic light scattering (DLS) was performed using Zetasizer Nano ZS (Malvern, England). The measurement was performed at room temperature (20 °C) using glass cuvette.

Chronoamperometric studies and cyclic voltammetry were performed with a PGSTAT 204 type electrochemical analyzer (Metrohm Autolab B.V., Switzerland) connected to a personal computer and controlled by NOVA 2.0 software. All voltammetry experiments were performed using the three-electrode system present on the SPEs, with an Ag/AgCl surface serving as the reference electrode and a platinum counter electrode surface around the working electrode surface. Chronoamperometric measurement was performed in phosphate buffer solution (50 mmol, pH=7.2). The cyclic voltammetry measurement was performed in 50 mM phosphate buffer solution (pH=7.2) using glass carbon electrode modified with black phosphorus quantum dots. All electrochemical potentials in this report are stated vs. the Ag/AgCl reference electrode. For the impedance electrochemical detection of gases, gold interdigitated electrodes (5 µm lines and spacing, purchased from DropSens) were coated with colloidal suspension of black phosphorus nanoparticles in DMF (16 000 rpm, 6 hours milling). Interdigitated electrodes were then left to dry for 15 minutes in vacuum oven. Impedimetric measurements were carried out using Autolab PGSTAT 204/ FRA 32M (Metrohm Autolab B.V., Switzerland). A sinusoidal potential modulation of 10 mV (at -0.1V to prevent BP oxidation and to achieve linearity conditions) was applied in the frequency range of 100 kHz to 0.1 Hz. Logarithmic scale of 10 points per decade was used.



Figure S1. Image (left) and diagram (right) of the equipment used for black phosphorous milling.



Figure S2. The STEM images of black phosphorus quantum dots after 48 hours sedimentation in DMF (3 hours milling). The scale bar corresponds to 100 nm (A), 250 nm (B) and 1000 nm (C).



Figure S3. The AFM images and corresponding height profiles of Line 1 and Line 2 of black phosphorus quantum dots after 48 hours sedimentation in DMF (3 hours milling).



Figure S4. The images of black phosphorus nanoparticles colloidal solution after milling for different hours (0.5 – 6 hours) and 48 hours sedimentation in various solvents and for different milling speed. Figure S3-A: NMP, 16 000 rpm; Figure S3-B: AN, 16 000 rpm; Figure S3-C: DIGLYM, 16 000 rpm; Figure S3-D: DMF, 11 000 rpm; Figure S3-E: DMF, 16 000 rpm.



Figure S5. The average particle size of black phosphorus nanoparticles colloidal solution after milling for different hours (0.5 – 6 hours) and 48 hours sedimentation in various solvents and for different milling speed and the yield of the milling in wt.%. Figure S3-A: NMP, 16 000 rpm; Figure S3-B: AN, 16 000 rpm; Figure S3-C: DIGLYM, 16 000 rpm; Figure S3-D: DMF, 16 000 rpm; Figure S3-E: DMF, 11 000 rpm.



Figure S6. The colloidal black phosphorus nanoparticles prepared by milling in acetonitrile separated by centrifugation and redispersed in DMF. Image taken after 7 day of sedimentation in DMF.



Figure S7. The particle size distribution measured by DLS and its integral value in black phosphorus quantum dots separated by sedimentation. DMF, 3 hours milling, 10 days sedimentation.



Figure S8. The cyclic voltammograms of glass carbon electrode modified with black phosphorus quantum dots prepared by 6 hours milling in DMF at 16 000 rpm. Phosphate buffer solution, 50 mmol, pH = 7.2, scan speed 100 mV/s. Potential stated against KCl saturated Ag/AgCl electrode.



DMF	Cube	DMF	Cube
16 krpm, 0.5 h	aproximation	16 krpm, 6 h	aproximation
Spike No.	l (nm)	Spike No.	l (nm)
1	959.1	1	1108.1
2	1916.8	2	368.2
3	2012.7	3	532.3
4	2097.0	4	466.4
5	1775.7	5	453.4
6	1303.2	6	617.2
7	1733.6	7	360.5
8	1796.8	8	563.6
9	1852.7	9	548.6
10	1310.3	10	718.4
11	1104.1	11	752.4
12	1250.5	12	463.3
13	1802.4	13	474.3
14	983.1		
15	1002.0		

Figure S9. The chronoamperograms of black phosphorus milled at 16 000 rpm in DMF for 0.5 hour and 6 hours and the table of its corresponding spikes calculated using cube shape approximation.



Figure S10. The chronoamperograms of black phosphorus milled at 11 000 rpm in DMF for 6 hours and the table of its corresponding spikes calculated using sphere shape approximation.



Figure S11. The impedance phase spectrum of methanol vapor at different concentrations (volume/volume). The black phosphorus detection limit of methanol is below 2500 ppm.