SUPPORTING INFO

Decoration of exfoliated black phosphorus with nickel nanoparticles and application in catalysis

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Experimental Section

Materials

All reactions were performed under nitrogen atmosphere using standard air-free techniques. Anhydrous dimethylsulfoxide, anhydrous dimethylformamide, hexane, trioctylphosphine (97%), Ni(acac)₂ (95%), oleylamine (70%) were used as received from Sigma Aldrich. Black phosphorus¹ and nickel nanoparticles²

were prepared according to literature procedures.

Preparation of few-layer black phosphorus (2D BP): Black phosphorus (BP) (5.0 mg) was put in a vial and dry dimethylsulfoxide (5.0 mL) and deoxygenated distilled water (3 μ L - 5 μ L) were added. The vial was sealed under nitrogen and exposed to ultrasound for 120 hours at a power of 200 W and 37 kHz. The sonication bath was constantly kept at 37 °C and in the dark. Afterwards, the vial was opened, degassed acetone was added (25.0 mL), and the suspension was centrifuged for 90 minutes at 6000 rpm. The colorless surnatant was removed, fresh acetone (25.0 mL) was added, and again the suspension was centrifuged at 6000 rpm for 90 min. The resulting dark grey powder was re-suspended by sonication (approximately one minute) in the desired organic solvent, (DMSO, THF, acetone, 2-propanol) and stored under nitrogen in the dark. The purity of the material was checked by ICP-MS.



Figure S1. Low-magnification image of BP flakes, anchored after dripping on Lacey carbon support film, imaged in TEM-BF mode.



Figure S2. Low-magnification STEM Z-contrast image of a stack of two BP flakes on Lacey carbon support film. (inset) Line intensity scan on higher magnified image showing the presence of only two BP flakes, as underlined by the two steps, the first step between the two flakes, and the second one between the lower flake and the vacuum.



Figure S3. STEM Z-contrast image at atomic resolution showing the crystalline structure of a BP flake



Figure S4. EELS spectrum of exfoliated black phosphorus flake. No oxygen is detected, indicating that the flake is not oxidized. The weak C K-edge peak arises from carbon supporting TEM grid.

Synthesis of Ni NPs.

To solid Ni(acac)₂ (50.0 mg, 0.194 mmol), oleylamine (640 μ L,1.362 mmol) and trioctylphosphine (70 μ L, 0.152 mmol) were added under nitrogen. The mixture was heated up to 220°C in 15 minutes under nitrogen and kept at this temperature for two hours, following a published procedure.² The average Ni NPs diameter was 11.4 nm with a standard deviation of 1 nm, see figure S5 below.



Figure S5. Bright field TEM image of Ni NPs and relative size distribution histogram. Scale bar: 100 nm.



Figure S6. Powder X-Ray diffraction of Ni NPs.



Figure S7. SAED (selected area electron diffraction) pattern of Ni NPs. The diffraction rings correspond to face-centered cubic nickel.

Immobilization of Ni NPs on phosphorene (Ni/2D BP)

All the samples used in the catalysis and shown in the pictures were prepared as follows:

To a freshly prepared suspension of few-layer BP in THF (1.2 mL, 1.2 mg, 0.0387 mmol "P") a black colloidal solution of nickel nanoparticles dispersed in toluene (0.29 mL, 0.018 M, 0.00531 mmol "Ni", P/Ni = 7.3) was added drop-wise under nitrogen at room temperature. After stirring for 30

minutes, degassed acetone (10.0 mL) was added, and the mixture was centrifuged at 8000 RPM for 20 minutes. The black residue was washed once more with acetone (10 mL), dried under a stream of nitrogen and re-suspended in THF. The Ni content of the isolated catalyst was measured by ICP-MS and resulted Ni to be 20.6 wt.%.

The same procedure was followed for the preparation of the catalyst having molar ratio P/Ni = 10.5, with a Ni content of 15.2% in weight as measured by ICP. The molar concentration of the colloidal solution of nickel nanoparticles was also assessed by ICP.



Figure S8. Bright field TEM image of Ni/2D BP, P: Ni molar ratio equal to 7.3:1 and relative size distribution histogram. Scale bar: 200 nm.



Figure S9. Energy dispersive X-ray spectrum of Ni/2D BP. The small peaks of C, O, and S can be attributed to a residual amount of DMSO. The Cu peaks originate from the Cu TEM grid on which the sample was placed.





Figure S10. a) Powder X-ray diffraction of exfoliated black phosphorus. b) Powder X-ray diffraction of Ni/2D BP. Inset of the region from $2\theta = 39^{\circ}$ to 47° , obtained after a prolonged acquisition. Peaks marked with a bar are characteristic of black P, the broad peak at $2\theta = 44.4^{\circ}$ is attributed to nickel.

Catalytic hydrogenations. In a typical experiment, a 50 mL stainless steel Parr reactor was equipped with a vial, containing a magnetic stirrer, and charged with a suspension of Ni NPs supported on 2D BP in tetrahydrofuran/toluene (3:1) under an inert atmosphere. Phenylacetylene was added, then the autoclave was sealed, purged with hydrogen (3 times) and then pressurized with hydrogen up to 10 bar. The autoclave was kept stirring at 80 °C in an oil bath preheated at 80 °C for the desired time. After that, the autoclave was cooled down to room temperature with ice and depressurized. Ultracentrifugation of the reaction mixture for 5 minutes at 10000 RPM allowed the heterogeneous catalyst to settle down. The colourless supernatant liquid was analyzed by gas chromatography and

mass spectrometry. To the black solid catalyst, a fresh solution of phenylacetylene in tetrahydrofuran/toluene (3:1) was added, and a new catalytic run was launched.

Entry	Conversion (%)	Selectivity to styrene (%)
Ni NPs	100.0	78.6
2D BP	0.0	0.0
Ni /2D BP	93.2	92.8

Table S1 Comparison of catalytic activity in the semihydrogenation of phenylacetylene.

Reaction conditions: 10 bar H₂, 80 °C, 1 hour, Ni NPs = 1.8 mol%, phenylacetylene: 0.30 mmol, 1.51 mg Ni/2D BP (20.6 wt% Ni). Both conversion and selectivity were evaluated by gas chromatography and gas chromatography interfaced with mass spectrometry (GC-MS).

Characterization

Transmission electron microscopy. TEM studies were carried out using a Philips instrument operating at an accelerating voltage of 100 kV. Few drops of the Ni NPs on 2D BP suspension in isopropanol were placed on the TEM lacey copper/carbon grid, air dried, and measured.

Atomic-resolution characterization by STEM was performed with a probe spherical aberrationcorrected JEOL ARM200CF, equipped with a Ceos hexapole-type Cs corrector, named CESCOR. The electron gun is a cold-field emission gun with an energy spread of 0.3 eV. The microscope was operated at a primary beam energy of 60 keV at which it is capable to deliver a probe size of 1.1 Å. Images were acquired in Z-contrast mode, by using the Gatan HAADF detector with a beam illumination angle of 33 mrad and a collection angle of 90 mrad. To improve the signal-to-noise ratio of the HAADF-STEM, a low-pass filtering of the images was applied. A last generation post-column energy filter, GIF Quantum ER, was used as EELS spectrometer, and EELS chemical maps were nearly simultaneously acquired to the HAADF-STEM images by using the 2D Spectrum Imaging (SI) capability.³ **Gas Chromatography** analyses were performed on a Shimadzu GC-14A gas chromatograph (with apolar column) equipped with flame ionization detector and a SPB-1 Supelco fused silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness).

Powder X-ray diffraction data were collected with an X'Pert PRO diffractometer with Cu-K α radiation ($\lambda = 1.5418$).

Raman spectroscopy was performed using a Renishaw inVia system equipped with a 532 nm laser and a motorised stage for 2D mapping of samples. A laser spot size of approximately 2 μ m in diameter was used.

UV-Vis absorption spectra were recorded using a Shimadzu 2600 spectrophotometer. Samples were tested using tetrahydrofuran as solvent in stoppered quartz cuvettes having 10 mm path length.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed with an Agilent 7700 Series spectrometer. Samples followed a microwave-assisted digestion in Nitric acid for trace analysis. Then, different dilutions of each sample with water for trace analysis were prepared, in order to obtain concentrations in the sensitivity range of the instrument for the elements under investigation (namely Ni and P). Standards at different concentrations have also been prepared and measured contextually to sample measurements, in order to obtain curve for each element under investigation.

Atomic force microscopy (AFM) measurements were performed with a Bruker Dimension Icon Atomic Force Microscope, in pick force mode. Samples for AFM were prepared by drop cast on a Si/SiO₂ substrate. The DMSO drop was left in contact with the substrate for 90 minutes, then the sample was washed with acetone and dried in vacuum overnight. Samples prepared with this method have almost no solvent traces, at least far from the edges, and quite small aggregates, as shown in Figure S11 (a). Nevertheless, re-aggregation of functionalized BP flakes could not be completely prevented during the deposition procedure. During AFM, we approached in regions where no aggregates were visible in the optical microscope, and found many small structures, shown in Figure S11 (b), which are likely to be single BP flakes or few flake-aggregates. These structures have a typical size of a few hundred nanometers and a thickness of up to 50nm, with a substrate coverage of 2-4%. An image of a typical flake is shown in the main text, in Figure 6.



Figure S11. (a) Optical microscopy image of a sample prepared for AFM by drop casting from a Ni/2D BP solution and (b) an AFM image (size $5\mu m \times 5\mu m$) of the same sample.



Figure S12. Bright field TEM images of pristine 2D BP. Left: freshly deposited BP flake on a TEM grid; right: the same flake that looks heavily degraded after one week exposure to ambient conditions in the dark. Scale bar: $1 \mu m$.

a)





Figure S13. a) Bright field TEM image of Ni/2D BP after catalytic tests, scale bar: 100 nm; and b) relative size distribution histogram.

¹ T. Nilges, M. Kersting, T. Pfeifer, J. Solid State Chem. 2008, 181, 1707-1711.

² S. Carenco, C. Boissière, L. Nicole, C. Sanchez, P. Le Floch, N. Mézailles, *Chem. Mater.* 2010, **22**, 1340-1349.

³ G. Nicotra, Q. M. Ramasse, I. Deretzis, A. La Magna, C. Spinella, F. Giannazzo *ACS Nano*, 2013, **7**, 3045-3052.