Layered Black Phosphorus as Reducing Agent – Decoration with Group 10 Metals

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Experimental

All synthetic experiments were conducted under protective atmosphere of nitrogen. PtCl\textsubscript{2}, PdCl\textsubscript{2} and K\textsubscript{2}PtCl\textsubscript{4} were purchased from Strem Chemicals, Inc. NiCl\textsubscript{2}.6H\textsubscript{2}O, aqueous ammonia (25 %), hydrochloric acid and acetonitrile were purchased from LachNer s.r.o, Czech Republic. All chemicals were used as received.

The high-resolution transmission electron spectroscopy (HRTEM) experiments were conducted using an EFTEM Jeol 2200 FS microscope (Jeol, Japan). A 200 keV acceleration voltage was used for the experiments. The elemental maps the EDS spectra were acquired using the SDD detector X-MaxN 80 TS from Oxford Instruments (GB). The samples were prepared by drop casting of a suspension of the material in acetone onto a TEM grid (Cu, 200 mesh) and its drying at room temperature.

X-ray powder diffraction data were collected using the Bruker D8 Discoverer (Bruker, Germany) powder diffractometer with the parafocusing Bragg–Brentano geometry using Cu\textsubscript{K}\textalpha\textsubscript{1} radiation (\(\lambda = 0.15418\) nm, \(U = 40\) kV, \(I = 40\) mA). Data were scanned over the angular range 5–90° (2\(\theta\)) with a step size of 0.019° (2\(\theta\)) and collected at room temperature. The data were evaluated with the Profex program.\[1\]

inVia Raman microscope (Renishaw, England) in backscattering geometry with CCD detector was used for Raman spectroscopy. DPSS laser (532 nm, 50 mW) with applied power 5 mW and a 50x magnification objective were used for the experiments. A silicon sheet was used to calibrate the instrument (peak position at 520 cm\textsuperscript{-1}) with resolution of less than 1 cm\textsuperscript{-1}. The samples were deposited on a stainless-steel sheet.

High-resolution X-ray photoelectron spectroscopy (XPS) was performed using a SPECS spectrometer equipped with an XR 50 MF monochromatic X-ray radiation source (1486.7 eV) and a Phoibos 150 2D CCD hemispherical analyzer and detector. The pressure inside the chamber during the experiments was 5\(\times\)10\textsuperscript{-10} mbar or lower. Wide-scan surveys were performed with Ep=80 eV, with subsequent high-resolution scans of the desired core lines with Ep=50 eV. The samples were placed on a double-sided carbon tape. The binding energy values are referenced to the adventitious carbon peak at 285 eV.

The NMR spectra were recorded using a Bruker AVANCE III spectrometer with the superconducting 400 MHz NMR Bruker ASCEND magnet equipped with a broadband cryoprobe with the \textsuperscript{31}P resonance frequency 162.33 MHz. The signal of 85% H\textsubscript{3}PO\textsubscript{4} in D\textsubscript{2}O was used as the external reference.

Black phosphorus was prepared from red phosphorus according to the Nigel’s procedure.\[2\] The crystals were subsequently exfoliated with high-energy shear force mill in acetonitrile under argon atmosphere for 10 hours. The as prepared material was decanted and dried in vacuo and stored in an argon filled glovebox.

Preparation of the BP-based materials

Nickel

NiCl\textsubscript{2}.6H\textsubscript{2}O (40 mg) was dissolved in demineralized water (15 ml) in a Schlenk flask and the light green solution was thoroughly de-oxygenated via repeated evacuation/nitrogen refill cycles. BP (50 mg) was added to the deaerated solution under a nitrogen counter-flow and the suspension was briefly sonicated for homogenization and subsequently stirred under nitrogen atmosphere at 70 °C.
for 24 h. The product was centrifugated, repeatedly washed/sonicated with deoxygenated water and finally washed with acetone and dried in vacuo to obtain 47 mg of the product (Ni-1).

In another experiment, NiCl₂.6H₂O (40 mg) was dissolved in demineralized water (15 ml) in a Schlenk flask and the solution was deaerated via repeated evacuation/nitrogen refill cycles. The solution was acidified with concentrated aqueous HCl (2 ml) and BP (50 mg) was added to it under a nitrogen counter-flow. The suspension was briefly sonicated to homogenize it and was subsequently stirred and heated under nitrogen atmosphere at 70 °C for 24 h. The solid was centrifugated, repeatedly washed/sonicated with deoxygenated water and finally washed with acetone and dried in vacuo to obtain 48 mg of the product. The analyses revealed that only the unmodified BP was isolated.

In the third experiment, NiCl₂ . 6H₂O (40 mg) was dissolved in concentrated aqueous ammonia solution (20 ml) in a Schlenk flask. The purplish solution was deaerated and BP (50 mg) was added under a nitrogen counter-flow. The suspension was briefly sonicated and stirred while heated at 70 °C for 24 h. The product was centrifugated, repeatedly washed/sonicated with deoxygenated water and subsequently washed with acetone and dried in vacuo to obtain 32 mg of the product (Ni-2).

**Palladium**

PdCl₂ (90 mg) was dissolved in acetonitrile (10 ml) in a Schlenk flask and the solution was thoroughly de-oxygenated via repeated evacuation/nitrogen refill cycles. BP (30 mg) was added under a nitrogen counter-flow and the suspension was briefly sonicated for homogenization and stirred under nitrogen atmosphere at 70 °C for 48 h. The product was centrifugated, repeatedly washed/sonicated with acetonitrile and finally washed with acetone and dried in vacuo to obtain 65 mg of the product (Pd-1).

In another experiment, PdCl₂ (30 mg) was suspended in demineralized water (15 ml) in a Schlenk flask and few drops of concentrated aqueous HCl were added in order to prepare a solution of PdCl₄²⁻. The orange solution was thoroughly de-oxygenated via repeated evacuation/nitrogen refill cycles. BP (50 mg) was added under nitrogen counter-flow and the suspension was stirred under nitrogen atmosphere at 70 °C overnight. The colorless mother liquor was decanted, the product was repeatedly washed/sonicated/centrifugated with demineralized water, and finally washed with acetone and dried in vacuo to obtain 62 mg of the product (Pd-2).

In the third experiment, PdCl₂ (30 mg) was suspended in concentrated aqueous ammonia solution in a Schlenk flask. The cloudy pinkish mixture became clear and colorless after 10 minutes. The solution was deaerated via repeated evacuation/nitrogen fill cycles and BP (50 mg) was added under nitrogen counterflow. The suspension was briefly sonicated and stirred and heated at 70 °C for 24 h. The product was centrifugated, repeatedly washed with deoxygenated water and finally with acetone and dried in vacuo to obtain 56 mg of the product (Pd-3).

**Platinum**

K₂PtCl₄ (40 mg) was dissolved in water (20 ml) in a Schlenk flask and the solution was thoroughly de-oxygenated via repeated evacuation/nitrogen refill cycles. BP (30 mg) was added under a nitrogen counter-flow and the suspension was briefly sonicated to homogenize the mixture. The resulting suspension was heated to 70 °C and stirred at this temperature under nitrogen atmosphere for 48 h. The initial red-violet color of the tetrachloroplatinate solution disappeared during the reaction. The colorless mother liquor was decanted, the product was repeatedly
washed/sonicated/centrifugated with demineralized water and finally washed with acetone and dried in vacuo to obtain 47 mg of the product (Pt-1).

In another experiment, PtCl$_2$ (25 mg) was dissolved in concentrated aqueous ammonia solution (20 ml) in a Schlenk flask and the solution was de-oxygenated. BP (30 mg) was added under a nitrogen counter-flow and the suspension was briefly sonicated for homogenization. It was subsequently heated to 70 °C and stirred under nitrogen atmosphere for 48 h. The colorless mother liquor was carefully decanted, the product repeatedly washed/sonicated/centrifugated with demineralized water and finally washed with acetone and dried in vacuo to obtain 46 mg of the product (Pt-2).

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Figure S1. HRTEM images (a, b), selected area diffraction pattern (c), distribution of the elements (d-f) and the XRD pattern (g) of the Ni-2 composite. Asterisk-labeled peaks represent BP diffractions.
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Figure S18. XPS survey spectrum of the material isolated after the reaction of NiCl₂ with BP in hydrochloric acid. The insets show the high-resolution spectra of the Ni 2p and P 2p regions. The C/O signals originate in the adventitious contamination.