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Supporting Information

Interfacial chemistry and electroactivity of black phosphorous decorated with transition metals

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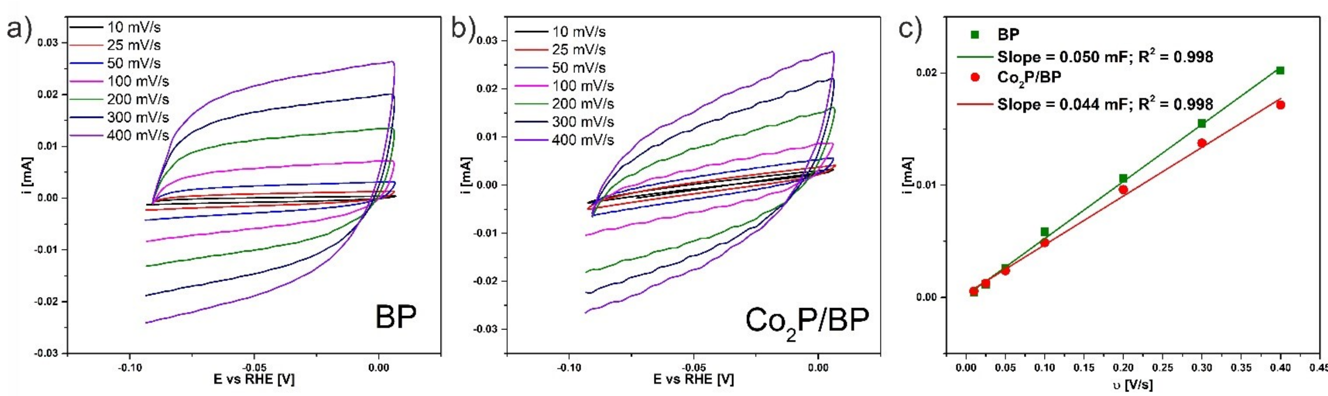

Figure S1. Cyclic voltammetry of (a) BP and (b) Co_2P/BP recorded in 0.5 M H_2SO4 at scan rates of 10, 25, 50, 100, 200, 300 and 400 mV/s; c) Capacitive current at -0.045 V vs RHE with scan rate for BP and Co_2P/BP.

Tungsten phosphide X-ray photoemission spectra description

The W-BP composite was prepared by evaporation of 1 ML metallic tungsten on BP film under UHV (see methods for details). Figure S1a shows a core level photoemission spectrum of P_{2p} before and after evaporation of W. The P_{2p} of W/BP composite can be deconvoluted with two doubles, one doublet at

129.6 eV compatible with pure BP, moreover, after close inspection a second doublet at lower BE energy (129.2 eV) can be observed, which can be associated with the formation of a tungsten phosphide. This is confirmed with the high-resolution W4f spectrum (Figure S1b) which can be deconvoluted with two doublets. One at higher BE energy (32.9 eV) can be inferred to WO_2, whose appearance can be associated with adventitious oxygen species present on the surface and metallic tungsten react with it during the growth process. The second doublet, which is the predominant one, is observed at 31.7 eV and indicate the $W^{\delta+}$ species ($0<\delta<3$) which can be assigned to W of WP.[1–3]

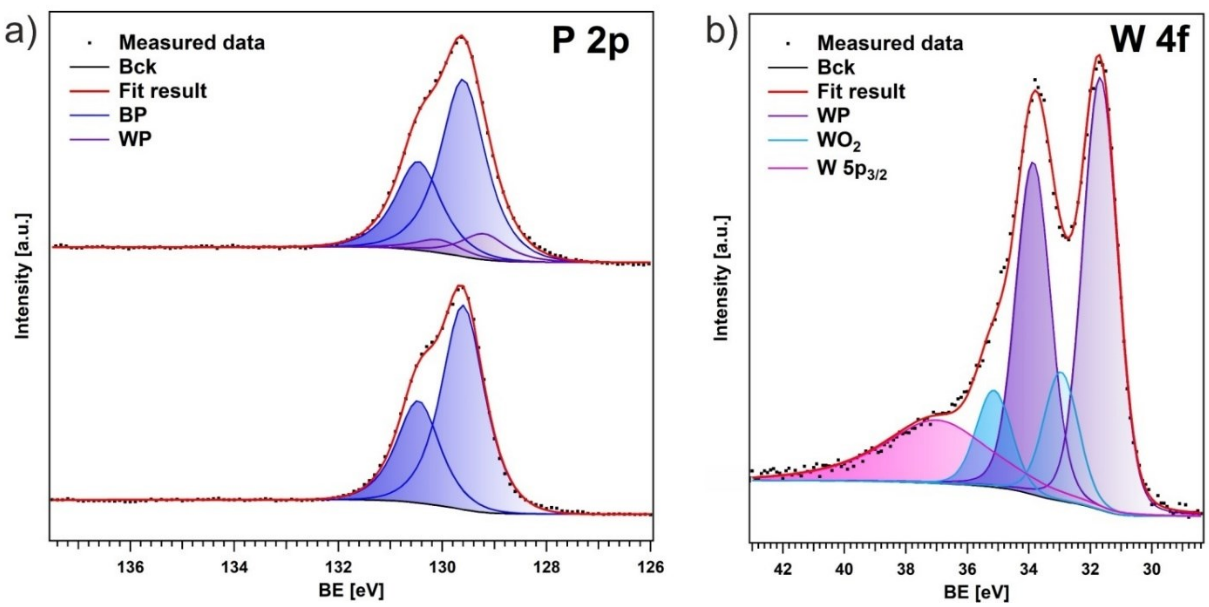

Figure S2. High resolution core-level XPS spectra of (a) P_{2p} before and after deposition of tungsten and (b) W_{4f} of W/BP composite.

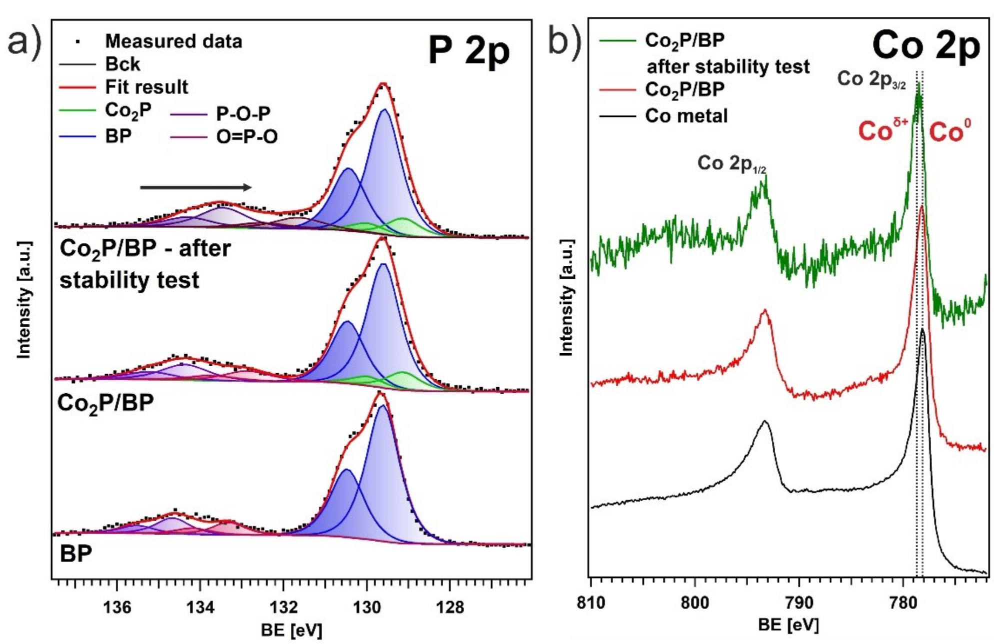

Figure S3. P 2p and Co 2p core-level XPS spectra before and after stability test of Co_2P/BP.

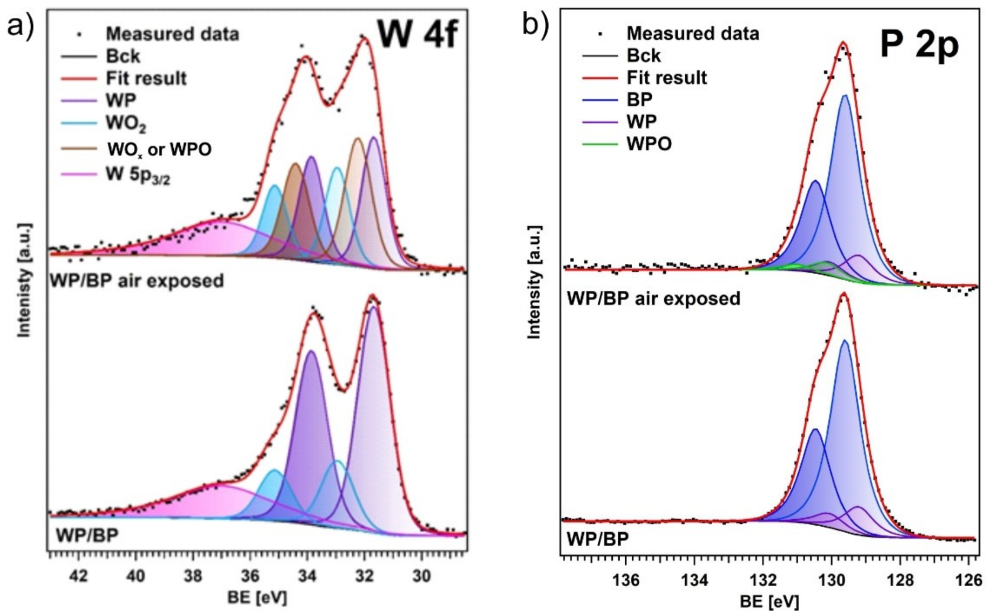

Figure S4. High resolution core-level XPS spectra of W_{4f} (a) and P_{2p} (b) before and after air exposition of W/BP composite.

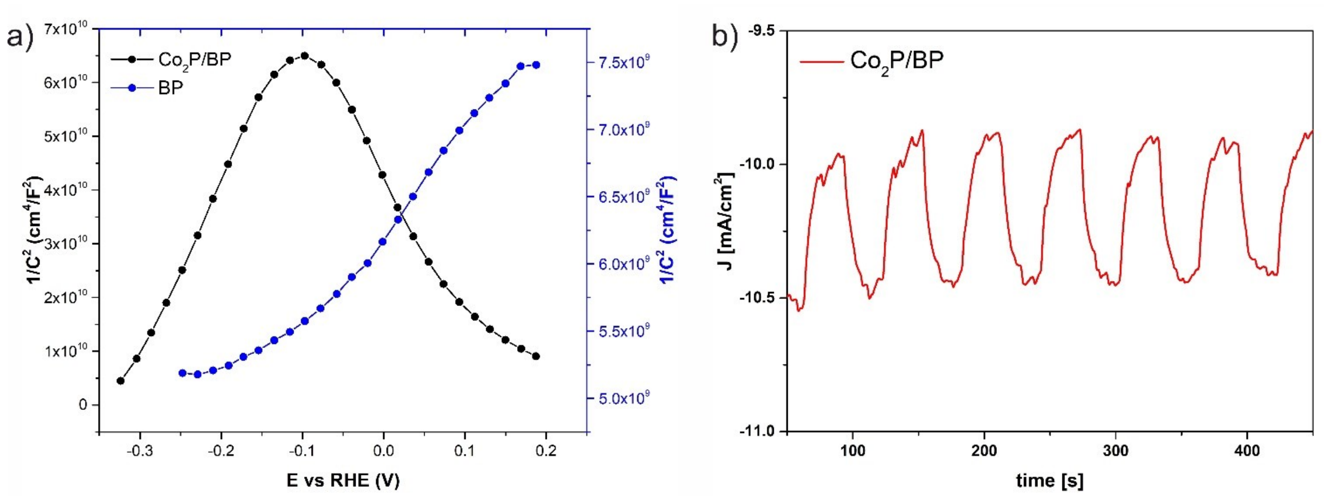

Figure S5. a) Mott-Schottky plot obtained from BP and Co_2P/BP samples; b) PEC respond for a Co_2P on black phosphorus sample measured at overpotential of $\eta = 0.305$ V vs RHE.

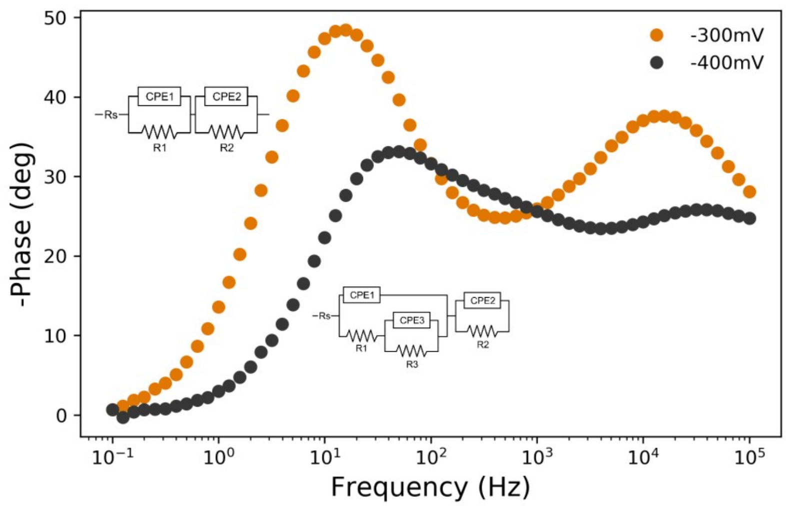

Figure S6. Phase angle plot showing the changes at the W/BP interface upon lowering the applied potential from -300 mV to -400 mV. The different equivalent circuits needed two fit the two spectra are also shown.

Table S1. Equivalent circuits used in the fitting of impedance spectra of Co/BP and values of the circuit components at different applied potential. For all parameter values, error was below 5%.

V (mV)	Rs (Ohm)	R1 (Ohm)	CPE1		R2 (Ohm)	CPE2		R3 (Ohm)	CPE3	
			n	P		n	P		n	P
-100	2	19	0.98	2E-8	11.8k	0.65	1E-5	8.6k	0.82	2E-5
-200	3	24	0.64	3E-6	133	0.65	1E-5	962	0.8	3E-6
-300	10	37	0.78	1E-6	64	1	1E-6	48	1	4E-7

Table S2. Equivalent circuits used in the fitting of impedance spectra of W/BP and values of the circuit components at different applied potential. A different circuit was used to fit the spectrum recorded at -400mV, as shown in the main article. For all parameter values, error was below 5%.

V (mV)	Rs (Ohm)	R1 (Ohm)	CPE1		R2 (Ohm)	CPE2		R3 (Ohm)	CPE3	
			n	P		n	P		n	P
-100	4	14555	0.85	1E-4	85	0.5	1E-4	-	-	-
-200	4	110	0.60	7E-5	10704	0.87	5E-5	-	-	-
-300	4	125	0.57	9E-5	2988	0.9	4E-5	-	-	-
-400	3	116	0.5	1E-4	44	0.7	1E-4	238	1	6E-5

[1] X. Zhang, T. Guo, T. Liu, K. Lv, Z. Wu, D. Wang, Electrochimica Acta Tungsten phosphide (WP) nanoparticles with tunable crystallinity , W vacancies , and electronic structures for hydrogen production, Electrochimica Acta. 323 (2019) 134798. doi:10.1016/j.electacta.2019.134798.
[2] Z. Tu, S. Mu, Ultrasmall tungsten phosphide nanoparticles embedded in nitrogen-doped carbon as a highly active and stable hydrogen-evolution electrocatalyst, J. Mater. Chem. A. 4 (2016) 15327–15332. doi:10.1039/c6ta05165k.
[3] Z. Xing, Q. Liu, A.M. Asiri, X. Sun, High-Efficiency Electrochemical Hydrogen Evolution Catalyzed by Tungsten Phosphide Submicroparticles, ACS Catalysis. 5 (2015) 145–149. doi:10.1021/cs5014943.