Supporting Information

Bandgap- and Local Field-Dependent Photoactivity of Ag/Black Phosphorus Nanohybrids

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Table S1. Calculated adsorption energy E_{ads} (eV), Ag-P bond length $d_{Ag\text{-}P}$ (Å) and average charge q_{Ag} of Ag (e) for Ag/P(010) tetralayer as a function of Ag coverage (θ)

θ (ML)	E_{ads} (eV/Ag atom)	$d_{Ag\text{-}P}$ (Å)	q_{Ag} (e/Ag atom)
1/4	-1.11	2.41	0.16
1/2	-1.35	2.51	0.05
1	-2.02	2.55	0.04
2	-2.30	2.57	0.00

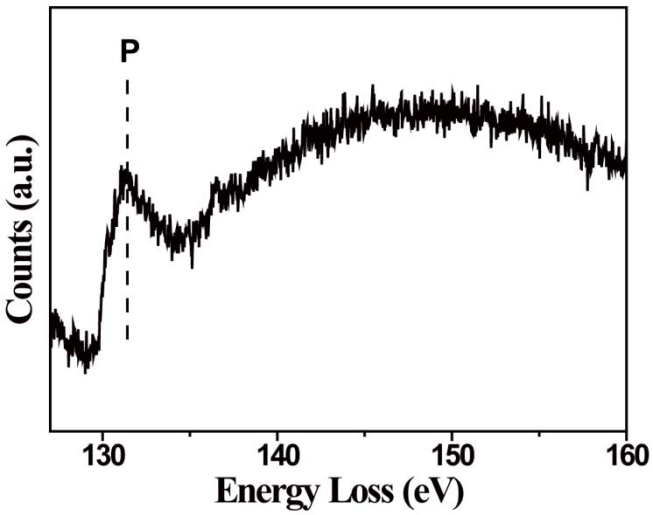

Figure S1. EELS spectrum of BP nanosheets.

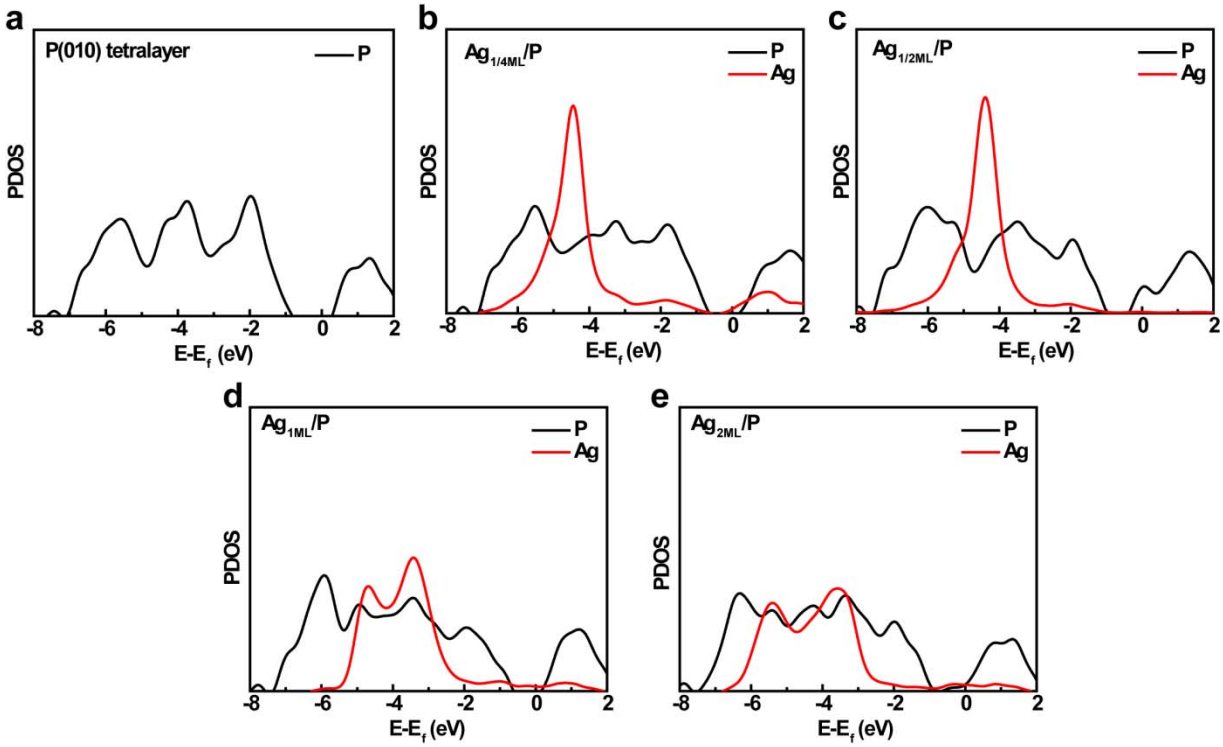

Figure S2. PDOS of Ag and P for Ag adsorption on a P(010) tetralayer. (a) P (010) tetralayer, (b) Ag $_{0.25ML}$/P, (c) Ag $_{0.5\ ML}$/P, (d) Ag $_{1\ ML}$/P, and (e) Ag $_{2\ ML}$/P.

To gain additional information about the interfacial interactions between Ag adlayers and BP support, PDOS were calculated (Figure S2). Both VB and CB of BP are mainly composed of P 2p states. In the range of Ag coverages (0.25-2 ML), Ag states mix with P 2p states. At low coverage (0.25 ML), Ag 4d states are localized and the ionic bond is formed between Ag 4d and P 2p. With the increasing Ag coverage up to 1-2 ML, Ag 4d states are more delocalized and hybridized with P 2p states. In other words, the covalent bond between Ag 4d and P 2p appears due to the populated Ag-Ag interactions. As a result, the metallic Ag becomes dominant.

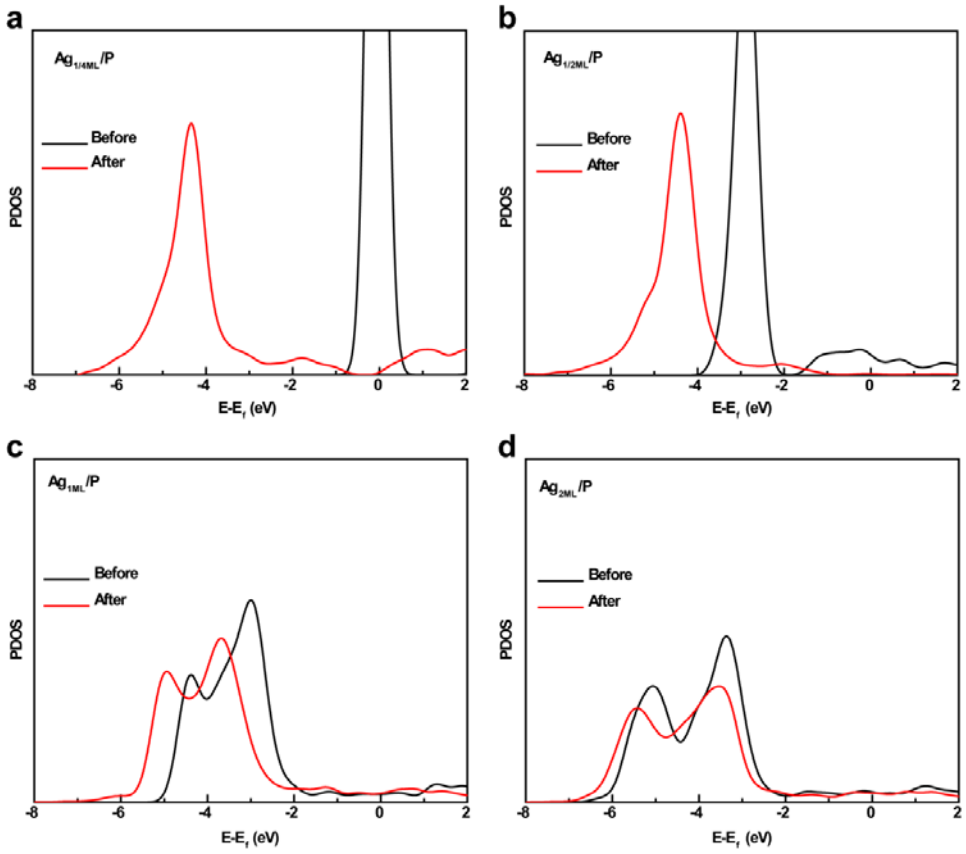

Figure S3. PDOS of Ag adlayers before and after deposition on a P(010) tetralayer.

Figure S3 displays that for gas-phase Ag nanostructures, the corresponding Ag PDOS is shifted downwards with increasing Ag content and Ag-Ag bond formation together with a peak broadening, indicating the presence of electron delocalization. When deposited onto BP, the Ag PDOS is dependent on the Ag coverage. At low Ag coverage (0.25 ML), the Ag-BP interaction leads to a significant down-shift by ~ 4.5 eV and the peak is broadened. In this case, the ionic bond is formed between Ag 4d and P 2p, resulting in the oxidation of Ag. Such effect is weakened when the coverage increases to 0.5 ML and the Ag-Ag bonds start to form, where the peak down-shift is only ~ 1.5 eV. In the range of 1-2 ML coverages, it becomes less pronounced with the further increase in Ag-Ag bond formation. The profile of Ag PDOS only changes slightly upon interaction with BP and the associated down-shift in PDOS decreases to ~ 0.5 eV at 1 ML and ~ 0.2 eV at 2 ML, respectively. Apparently, the covalent nature appears and dominates at the Ag-BP interface.

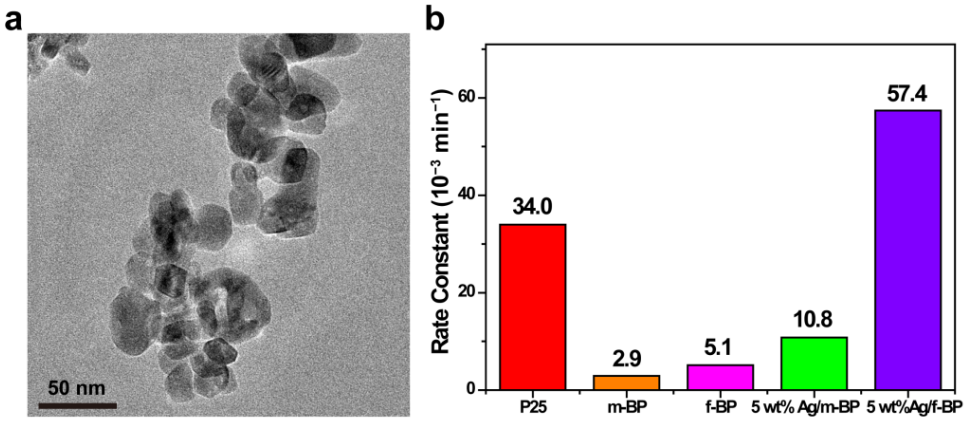

Figure S4. (a) Typical TEM image of P25. (b) Photoactivity of P25, m-BP, f-BP, 5 wt% Ag/m-BP and 5 wt% Ag/f-BP samples.

Figure S4a is a typical TEM image of P25, showing the particle size is about 20-30 nm. And the photoactivity is displayed in Figure S4b. The reaction rate constant of P25 is 34.0 × 10^{-2} min^{-1}, which is 11.7-fold, 6.7-fold and 3.1-fold larger than that of m-BP, f-BP, 5 wt% Ag/m-BP, respectively. However, the reaction rate of 5 wt% Ag/f-BP is 57.4 × 10^{-2} min^{-1}, 1.6-fold larger than that of P25.

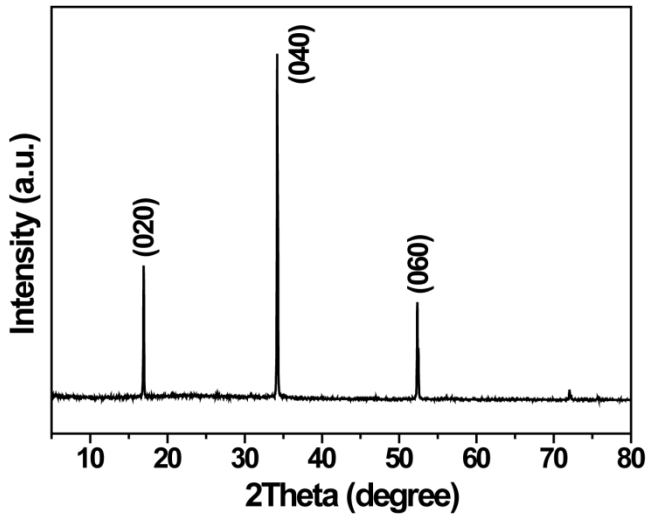

Figure S5. XRD patterns of bulk-like BP crystals.