



Rational Design and Preparation of S-Scheme Heterojunction Photocatalysts for Photocatalytic Hydrogen Production

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Abstract

Growing global energy demand and environmental concerns have intensified the need for sustainable technologies such as photocatalytic hydrogen production, which directly converts solar energy into a clean, high-density fuel. Two-dimensional (2D) semiconductors particularly ,Group 15 pnictogens ,are attractive photocatalysts due to their large surface areas and distinctive electronic properties. However, limited light absorption and rapid electron–hole recombination restrict their photocatalytic efficiency. S-scheme heterojunctions overcome these limitations by enhancing light absorption and promoting efficient charge-carrier separation. BiVO₃ is an important photocatalyst with strong oxidation capability arising from its favorable band structure. Herein, an S-scheme phosphorene/BiVO₃ heterojunction was constructed by coupling 2D phosphorene with BiVO₃ prepared via liquid-phase self-assembly. This heterojunction was characterized by structural, morphological, and optical techniques. An internal electric field effectively suppressed charge carrier recombination while preserving phosphorene's strong reduction capability and BiVO₃'s oxidation capability, enhancing overall photocatalytic activity. To optimize performance, S-scheme BiVO₃/phosphorene heterojunctions with phosphorene loading ratios of 25%, 50%, and 75% were synthesized and their hydrogen evolution systematically compared. The 75% phosphorene heterojunction exhibited the highest photocatalytic hydrogen production after an eight-hour reaction. These findings demonstrate the developed heterojunction is a promising photocatalyst for solar-driven hydrogen production.

Experimental Section

Synthesis of BiVO₃: Equimolar amounts of bismuth nitrate and sodium metavanadate (5 mmol each) were mixed in ethylene glycol and ultrasonicated (300 W) for 45 min. The precipitate was filtered, washed with deionized water, and dried at 140 °C for 24 h.

Synthesis of phosphorene/BiVO₃ heterojunction: The phosphorene/BiVO₃ heterojunction was prepared via liquid-phase self-assembly. BiVO₃ and exfoliated phosphorene were sonicated in a polar solvent for 5 h, followed by overnight stirring under an Ar atmosphere. The final product was centrifuged, washed with ethanol, and dried at 40 °C for 12 h.

Photocatalytic hydrogen evolution experiments: In the dye-sensitized photocatalytic hydrogen evolution experiments, 10 mg of catalyst was used together with eosin-Y (0.33 mM) as photosensitizer and TEOA (5%) as sacrificial electron donor. The TEOA and sensitizer solutions were sonicated and purged with N₂ to remove oxygen, then combined with the catalyst in a 135 mL quartz cell and sealed under anaerobic (glovebox) conditions. The sealed cell was irradiated for 8 h under visible light at room temperature with continuous magnetic stirring. Headspace gas samples were withdrawn hourly, and the evolved hydrogen was quantified by gas chromatography (Shimadzu GC-2010Plus, Ar carrier gas).

Results and Discussion

1-Morphological Characterization

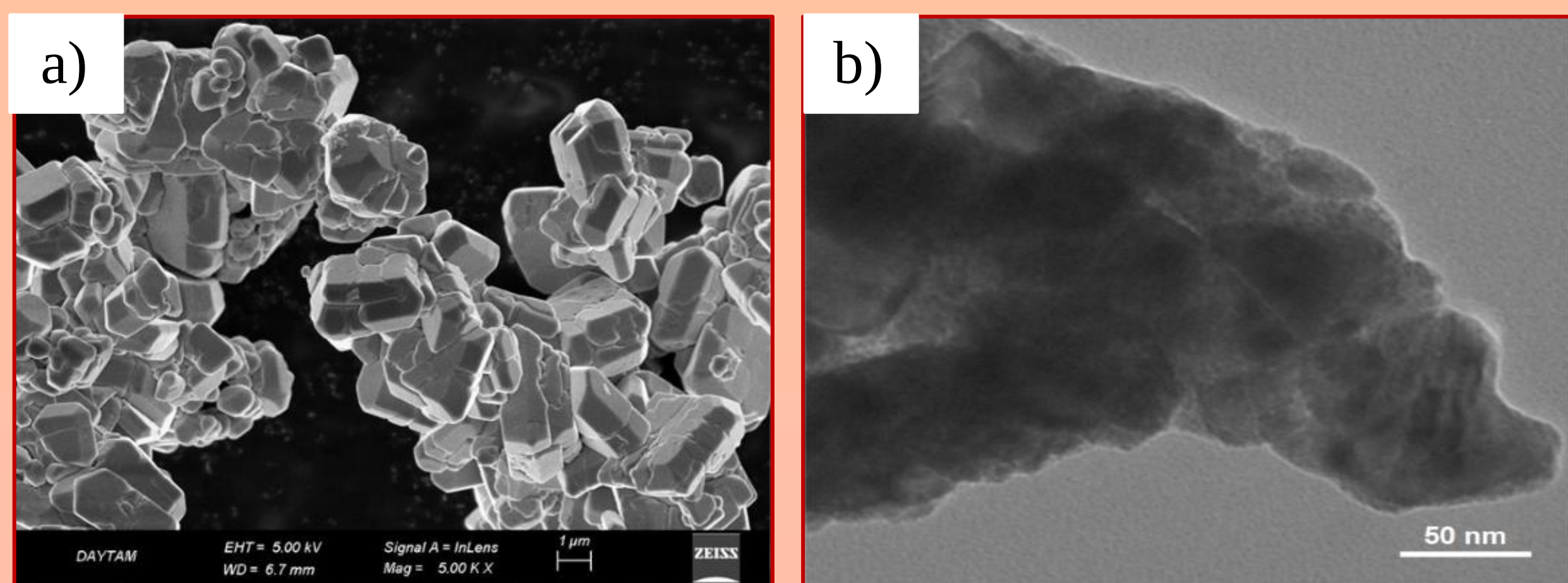


Figure 1. Morphological analysis of the pure BiVO₃ photocatalyst: (a) SEM image showing highly crystallized, smooth-surfaced uniform structures with a width of approximately 3 μm, and (b) TEM image showing rod-like and irregular particles.

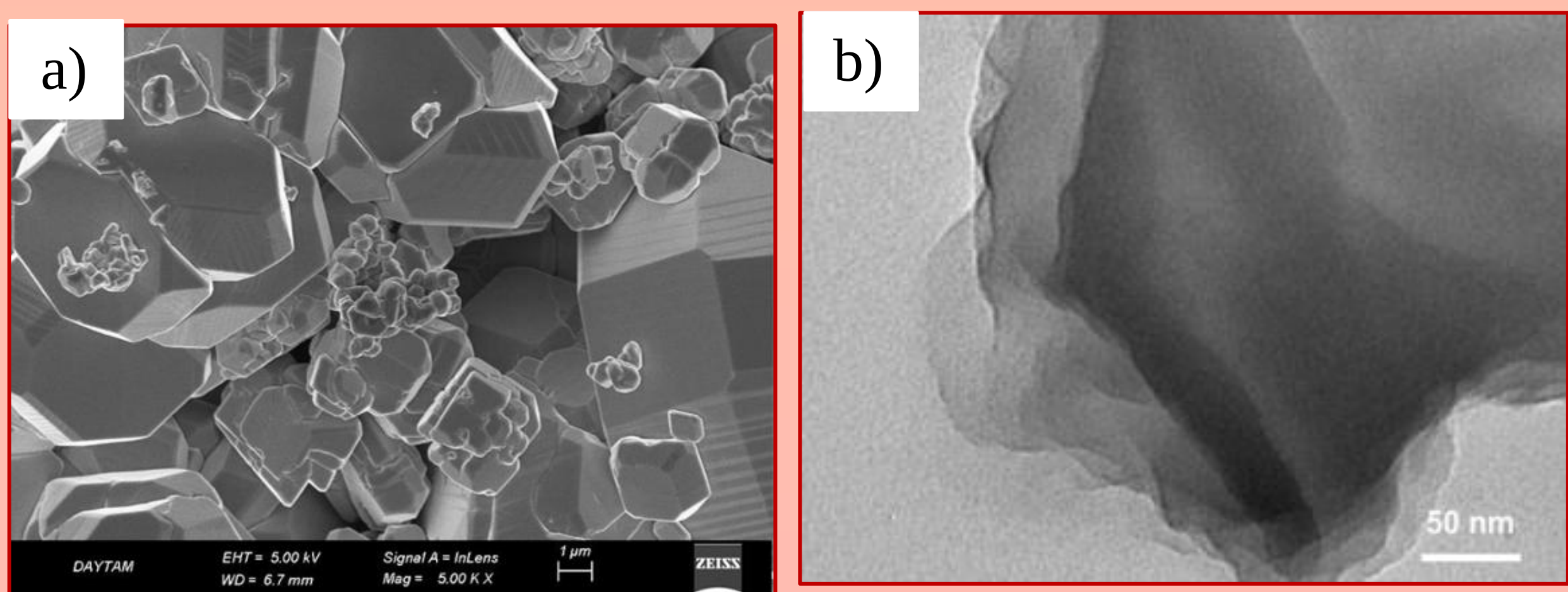


Figure 2. Morphological analysis of the phosphorene/BiVO₃ heterojunction: (a) SEM image showing phosphorene nanosheets anchored on BiVO₃ structures, and (b) TEM image suggesting close interfacial contact between the 2D phosphorene and BiVO₃ nanoplates.

2-Structural Characterization

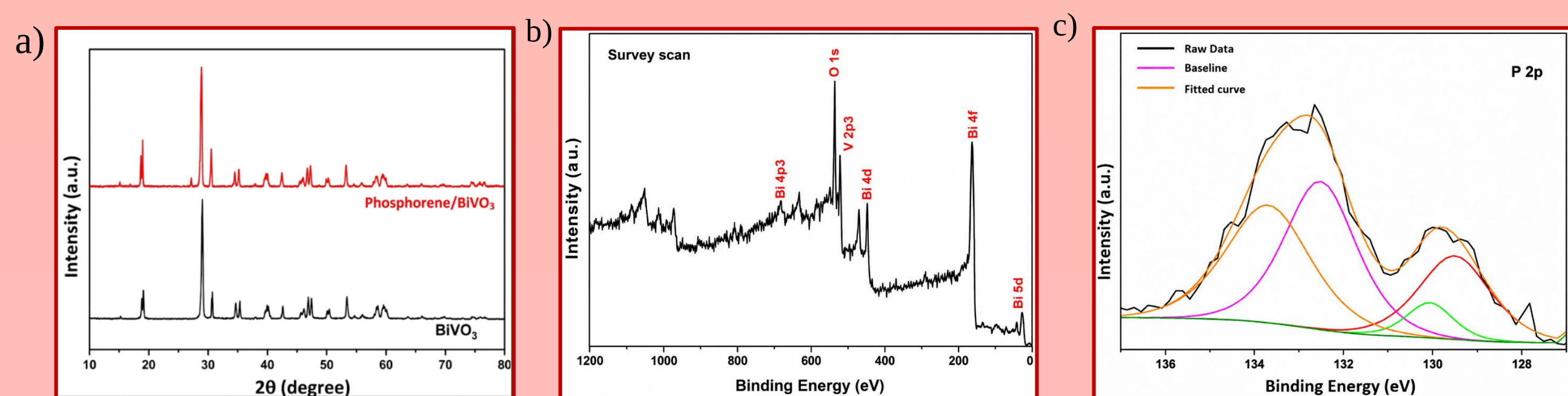


Figure 3. (a) XRD patterns of pure BiVO₃ and the phosphorene/BiVO₃ heterojunction. XPS spectra of the composite: (b) survey scan, and (c) high-resolution P 2p spectrum. The patterns confirm the successful integration of phosphorene without impurity peaks, while the P 2p spectrum validates strong interfacial chemical bonding.

3-Optical Properties

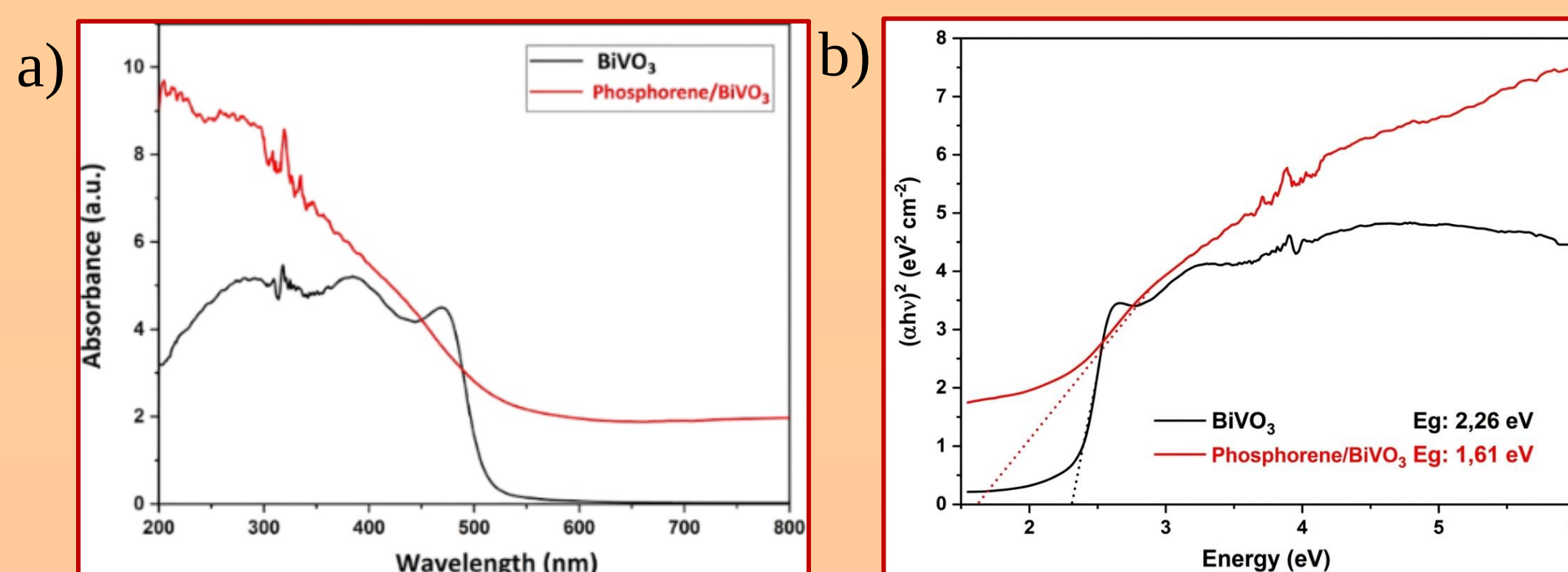


Figure 4. (a) UV-Vis DRS spectra and (b) corresponding Tauc plots of pure BiVO₃ and the phosphorene/BiVO₃ heterojunction. The estimated optical band gap decreased from 2.26 eV to 1.61 eV upon the integration of phosphorene, significantly expanding the visible-light absorption capacity.

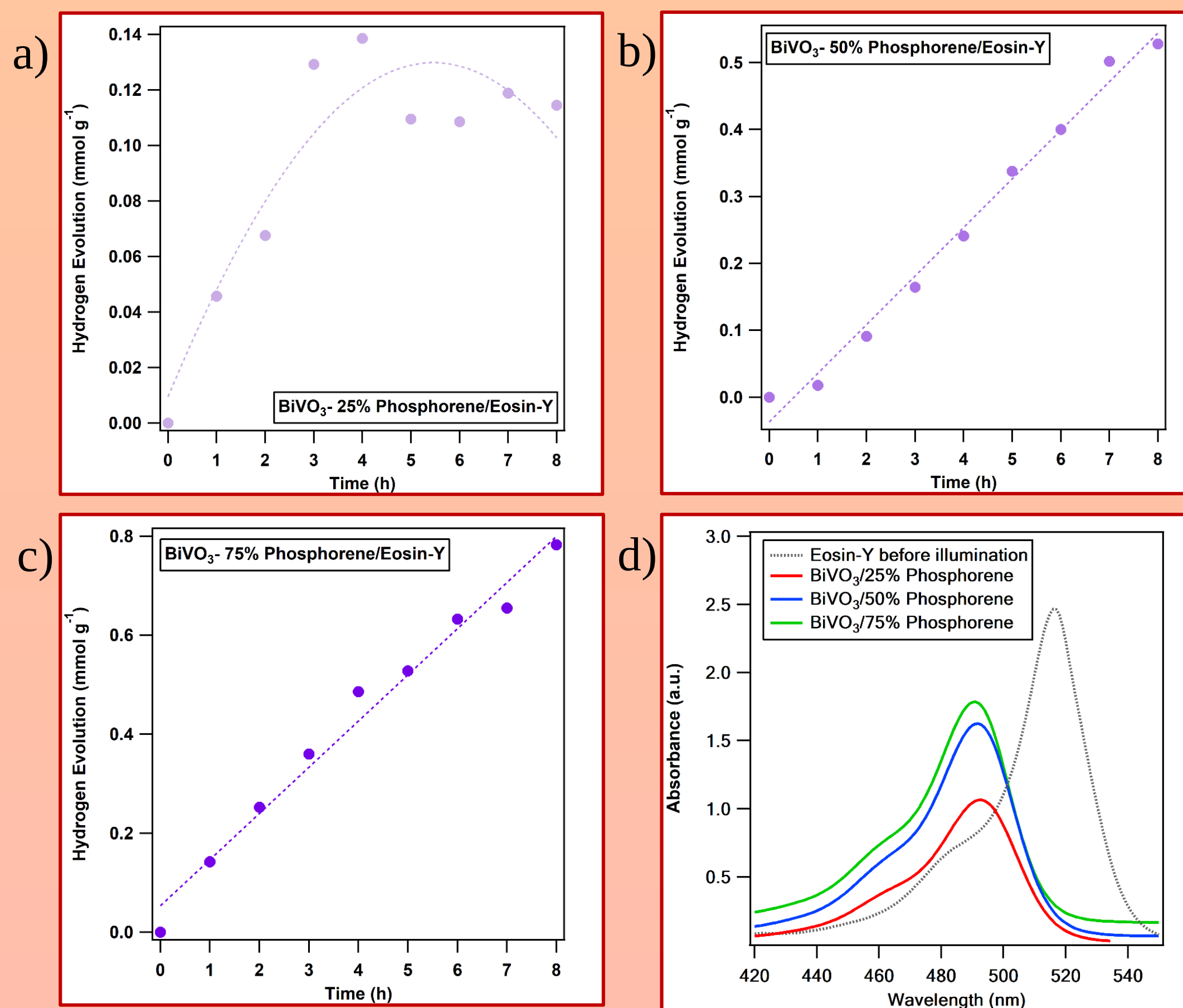


Figure 5. Photocatalytic H₂ evolution of phosphorene/BiVO₃ heterojunctions with phosphorene loadings of (a) 25%, (b) 50%, and (c) 75%. The 75% sample exhibited the highest H₂ evolution rate under the tested conditions (d) UV-vis absorption spectra of Eosin-Y after the photocatalytic reactions.

Conclusion

Successful synthesis of the heterojunction: XRD, XPS, SEM, and TEM analyses confirmed the successful formation of the phosphorene/BiVO₃ heterojunction via the liquid-phase self-assembly method. Notably, XPS results strongly validated the interfacial chemical bonding between the 2D phosphorene nanosheets and BiVO₃ nanoplates, which is consistent with the proposed S-scheme charge-transfer pathway. **Extended visible-light absorption:** Integrating phosphorene narrowed the band gap from 2.26 eV (pure BiVO₃) to 1.61 eV, substantially broadening the visible-light harvesting capacity of the heterojunction.

75% phosphorene as the optimal loading ratio: Comparing 25%, 50%, and 75% phosphorene-loaded heterojunctions, the 75% sample exhibited the highest photocatalytic H₂ production over the 8-hour reaction period, perfectly correlating with its minimal Eosin-Y dye degradation.

Future Outlook: These findings establish the phosphorene/BiVO₃ S-scheme heterojunction as a promising, further-optimizable photocatalyst for sustainable, solar-driven hydrogen production.

Acknowledgment

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