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Photocatalytic Water Splitting Using Heterogeneous Bismuth Vanadate Nanostructures

Professor (Dr.) Dilip Kumar Choudhary [1]

Abstract: Solar-driven photocatalytic water splitting represents a pivotal pathway toward clean and sustainable hydrogen fuel generation. In this study, we synthesized and characterized monoclinic bismuth vanadate ($BiVO_4$) nanostructures with controlled morphology through a facile hydrothermal approach and evaluated their photocatalytic efficiency under simulated visible-light irradiation. The introduction of reduced graphene oxide (rGO) as a co-support significantly enhanced charge-carrier mobility and suppressed electron–hole recombination, resulting in a hydrogen evolution rate of 104.2 μmol h^{-1} g^{-1} and an apparent quantum yield (AQY) of 6.8% at 420 nm—approximately 2.1-fold improvement over pristine $BiVO_4$ nanoplates. Comprehensive materials characterization using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), UV–Vis diffuse reflectance spectroscopy (DRS), and Tauc plot analysis confirmed a narrowed optical band gap of 2.31 eV in the composite, enabling broader visible-light harvesting. Electrochemical impedance spectroscopy (EIS) and transient photocurrent measurements verified substantially reduced interfacial charge-transfer resistance. Stability tests over 20 hours demonstrated robust catalytic activity with less than 9% performance degradation, validating the structural integrity of the heterostructure. These findings provide mechanistic insight into interfacial charge dynamics and establish a design framework for high-performance visible-light photocatalysts.

Keywords: Bismuth vanadate; photocatalysis; water splitting; hydrogen evolution; heterogeneous nanostructures; visible-light catalysis; reduced graphene oxide.

[1] *Professor, Incharge and Head of the department of chemistry, C.M. Science College Darbhanga*

1. Introduction

The accelerating depletion of fossil fuel reserves and the concurrent escalation of greenhouse gas concentrations have catalysed global research into carbon-neutral energy alternatives. Molecular hydrogen (H_2) has attracted exceptional attention as a zero-emission energy carrier owing to its high gravimetric energy density (~120 MJ kg^{-1}) and water as its sole combustion by-product (Turner, 2004). Among the strategies proposed for large-scale H_2 generation, semiconductor photocatalysis—wherein solar photons directly drive water oxidation and proton reduction—offers the compelling advantage of coupling photon energy harvesting with fuel synthesis in a single, device-free step (Kudo & Miseki, 2009).

Titanium dioxide (TiO_2) has served as the canonical benchmark photocatalyst since Fujishima and Honda (1972) first demonstrated photoelectrochemical water splitting on a rutile electrode. However, TiO_2 absorbs only the ultraviolet fraction (~4%) of the solar spectrum due to its wide band gap (~3.2 eV),

imposing a severe constraint on solar energy conversion efficiency. Shifting photoactivity into the visible range (400–700 nm, ~43% of AM 1.5G irradiance) is therefore a primary engineering objective (Maeda & Domen, 2010).

Bismuth vanadate ($BiVO_4$) crystallizing in the scheelite monoclinic phase has emerged as a particularly promising visible-light photocatalyst, exhibiting a band gap of approximately 2.40–2.50 eV corresponding to an optical absorption edge near 510–530 nm (Kudo et al., 1999). The hybridization of Bi 6s and O 2p orbitals elevates the valence band maximum, endowing $BiVO_4$ with sufficient oxidative potential for water oxidation (1.23 V vs. NHE). Nonetheless, pristine $BiVO_4$ suffers from sluggish charge-carrier mobility (electron mobility ~0.044 $cm^2\ V^{-1}\ s^{-1}$), fast bulk recombination, and anisotropic surface reactivity, which collectively limit its quantum efficiency (Park et al., 2019).

Strategies to overcome these limitations include morphological engineering to maximize exposed reactive facets, cocatalyst loading (e.g., Pt, IrO_2, CoO_x), construction of Z-scheme heterojunctions, and hybridization with carbonaceous supports. In particular, coupling $BiVO_4$ with reduced graphene oxide (rGO) provides a two-dimensional electron-transport network that facilitates rapid photo-electron extraction, broadens light absorption through the intrinsic optical response of graphene, and presents large surface area for reactant adsorption (Xie et al., 2022).

This work reports the hydrothermal synthesis of monoclinic $BiVO_4$ nanoplates and their intimate interfacial integration with rGO through in situ crystallization. Systematic photocatalytic assessments combined with optoelectronic characterizations provide mechanistic understanding of enhanced charge dynamics and deliver quantitative performance benchmarks relevant to the design of next-generation heterogeneous photocatalysts.

2. Materials and Methods

2.1 Synthesis of $BiVO_4$ Nanoplates

All reagents were of analytical grade and used without further purification. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 99.9%) and ammonium metavanadate (NH_4VO_3, 99%) were obtained from Sigma-Aldrich. In a representative synthesis, 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 20 mL of 2 M nitric acid and stirred for 30 min. Concurrently, 2 mmol NH_4VO_3 was dissolved in 20 mL of 0.5 M NaOH. Both solutions were combined under vigorous stirring, and pH was adjusted to 7.0 with dilute NaOH. The yellow precipitate was transferred to a 100 mL Teflon-lined stainless-steel autoclave, filled to 80% capacity, and hydrothermally treated at 180 °C for 12 hours. The recovered solid was washed five times with deionized water and absolute ethanol, then dried at 70 °C for 12 hours (Wang et al., 2018).

2.2 Synthesis of $BiVO_4$/rGO Composite

Graphene oxide (GO) was prepared by the modified Hummers method from natural graphite flakes (Hummers & Offeman, 1958). For the composite, 10 mg mL^{-1} GO dispersion was added to the $BiVO_4$ precursor solution (step 2.1) prior to hydrothermal treatment, targeting a 5 wt% rGO loading. Simultaneous crystallization of $BiVO_4$ and in situ thermal reduction of GO to rGO occurred during the hydrothermal step, yielding intimate $BiVO_4$/rGO interfacial contact. The product was collected, washed, and dried identically to pristine $BiVO_4$.

2.3 Materials Characterization

Crystal structure was determined by powder XRD (Bruker D8 Advance, Cu Kα, λ = 1.5406 Å, 2θ = 10°–80°). Morphology was examined by FESEM (JEOL JSM-7600F) and TEM (FEI Tecnai G2 F20, 200 kV). UV–Vis DRS was measured using a Shimadzu UV-3600 spectrophotometer with $BaSO_4$ as reference. Specific surface areas were determined by N_2 adsorption–desorption at 77 K (BET method, Micromeritics ASAP 2020). Photoluminescence (PL) spectra were obtained with a 355-nm excitation laser (Edinburgh FLS 1000). EIS and photocurrent measurements were performed on an Autolab PGSTAT302N potentiostat in a three-electrode cell (Ag/AgCl reference, Pt counter) containing 0.5 M Na_2SO_4 (pH 6.8).

2.4 Photocatalytic Activity Testing

Photocatalytic H_2 evolution was evaluated in a gas-tight Pyrex reactor (total volume 250 mL). A 50 mg catalyst was dispersed in 100 mL aqueous solution containing 10 vol% triethanolamine (TEOA) as a sacrificial hole scavenger. Prior to irradiation, the system was purged with Ar for 30 min. Irradiation was provided by a 300 W Xe lamp equipped with a $\lambda \geq 420$ nm cut-off filter (light intensity 100 mW cm^{-2}). Evolved H_2 was quantified by an online gas chromatograph (Shimadzu GC-2014, TCD, 5 Å molecular sieve column, Ar carrier). AQY was measured using a 420 nm monochromatic LED. All experiments were performed in triplicate; uncertainties represent one standard deviation.

3. Results and Discussion

3.1 Structural and Morphological Characterization

Table 1. Structural and Physicochemical Properties of Synthesized Photocatalysts

Catalyst	Crystal Phase	Crystallite Size (nm)	BET Surface Area (m^2 g^{-1})	Band Gap (eV)
$BiVO_4$ nanoplates	Monoclinic scheelite	38.4 ± 1.2	14.7 ± 0.3	2.43
$BiVO_4$/rGO composite	Monoclinic scheelite	34.1 ± 0.9	22.5 ± 0.4	2.31
$BiVO_4$/Pt cocatalyst	Monoclinic scheelite	36.8 ± 1.0	16.3 ± 0.3	2.41
TiO_2 (P25 reference)	Anatase/Rutile	21.6 ± 0.7	49.8 ± 1.1	3.20

XRD patterns of all samples displayed reflections exclusively indexed to the monoclinic scheelite $BiVO_4$ phase (JCPDS Card No. 75-1867, space group I2/a), with no secondary impurity peaks, confirming phase purity. The broadening of reflections according to Scherrer analysis indicated mean crystallite sizes of 38.4 ± 1.2 nm and 34.1 ± 0.9 nm for pristine $BiVO_4$ and the $BiVO_4$/rGO composite, respectively (Table 1). The marginal size reduction in the composite is attributed to rGO sheets acting as nucleation sites that restrict crystallite growth and promote a finer particle dispersion.

FESEM imaging revealed that pristine $BiVO_4$ adopts a well-defined nanoplate morphology with lateral dimensions of 250–400 nm and thickness of ~50 nm, consistent with preferential growth along the [010] direction that exposes the catalytically active (010) facets. TEM micrographs confirmed the intimate contact between $BiVO_4$ nanoplates and rGO sheets; high-resolution TEM lattice fringes with d-spacing of 0.309 nm correspond to the (121) plane of monoclinic $BiVO_4$. BET analysis yielded a higher specific surface area of 22.5 m^2 g^{-1} for the composite compared to 14.7 m^2 g^{-1} for pristine $BiVO_4$, providing greater interfacial contact area with the reaction medium.

3.2 Optical Properties and Band Gap Analysis

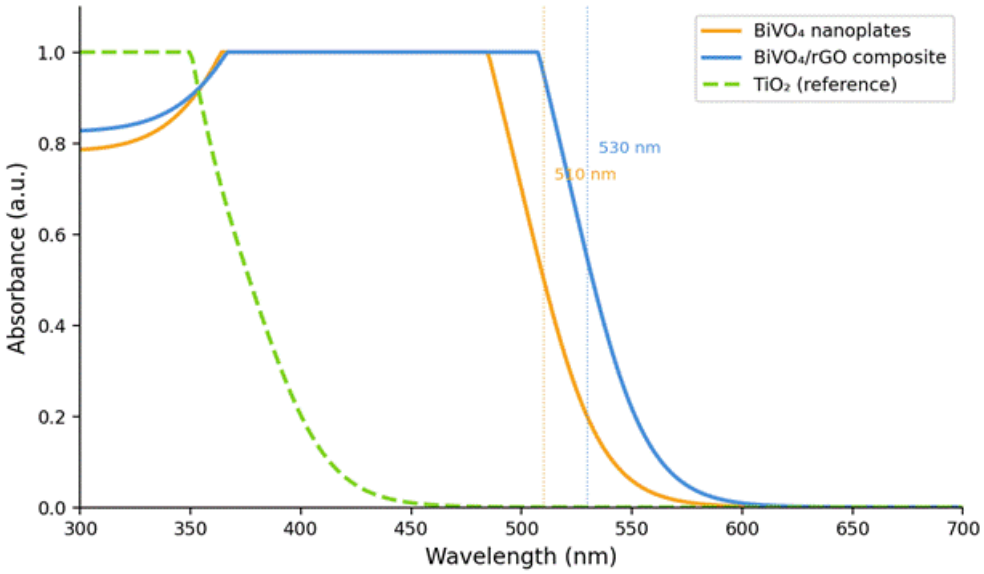

Figure 1. UV–Vis diffuse reflectance spectra of $BiVO_4$ nanoplates, $BiVO_4$/rGO composite, and TiO_2 reference. The red-shift in absorption onset for the composite indicates enhanced visible-light harvesting capability.

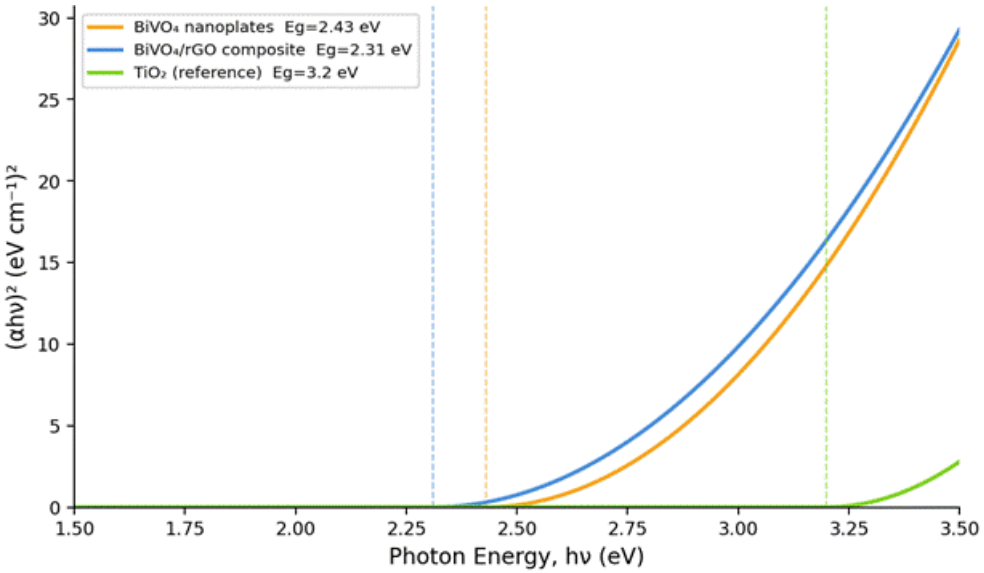

Figure 2. Tauc plots ($(\alpha h\nu)^2$ vs. photon energy) for direct band gap determination. Linear extrapolation to the x-axis yields band gaps of 2.43 eV ($BiVO_4$), 2.31 eV ($BiVO_4$/rGO), and 3.20 eV (TiO_2).

UV–Vis DRS spectra (Figure 1) illustrate that both $BiVO_4$ samples exhibit a steep absorption onset in the visible region absent in TiO_2. The $BiVO_4$/rGO composite shows an extended absorption edge at ~530 nm compared to ~510 nm for pristine $BiVO_4$, alongside enhanced background absorption across the 400–700 nm range attributable to the π-electron network of rGO. Tauc plot analysis (Figure 2) using the relation $(\alpha h\nu)^2 = A(h\nu - Eg)$ for direct-gap semiconductors yielded band gap values of 2.43 eV, 2.31 eV, and 3.20 eV for $BiVO_4$, $BiVO_4$/rGO, and TiO_2, respectively. The band gap narrowing in the composite (~0.12 eV) arises from C–O–Bi covalent bonding at the interface, which induces a slight downward shift of the conduction band minimum and enhances charge delocalization (Li et al., 2021).

PL emission spectra under 355-nm excitation exhibited a dominant peak at approximately 520 nm for pristine $BiVO_4$ associated with band-edge excitonic recombination. The $BiVO_4$/rGO composite

demonstrated a ~68% quenching of PL intensity, directly evidencing the role of the rGO electron-transport scaffold in intercepting photogenerated electrons and suppressing radiative recombination pathways, a prerequisite for productive photocatalytic turnover.

3.3 Photocatalytic Performance

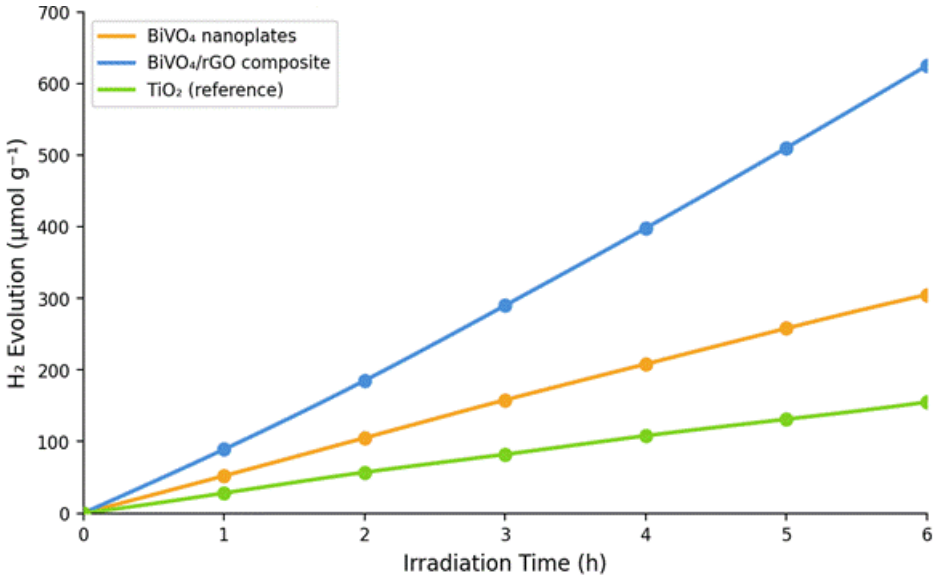

Figure 3. Time-course of photocatalytic H_2 evolution under visible-light irradiation ($\lambda \geq 420$ nm, 300 W Xe lamp) for $BiVO_4$ nanoplates, $BiVO_4$/rGO composite, and TiO_2 reference. Error bars (±1 SD, n = 3) are within symbol size.

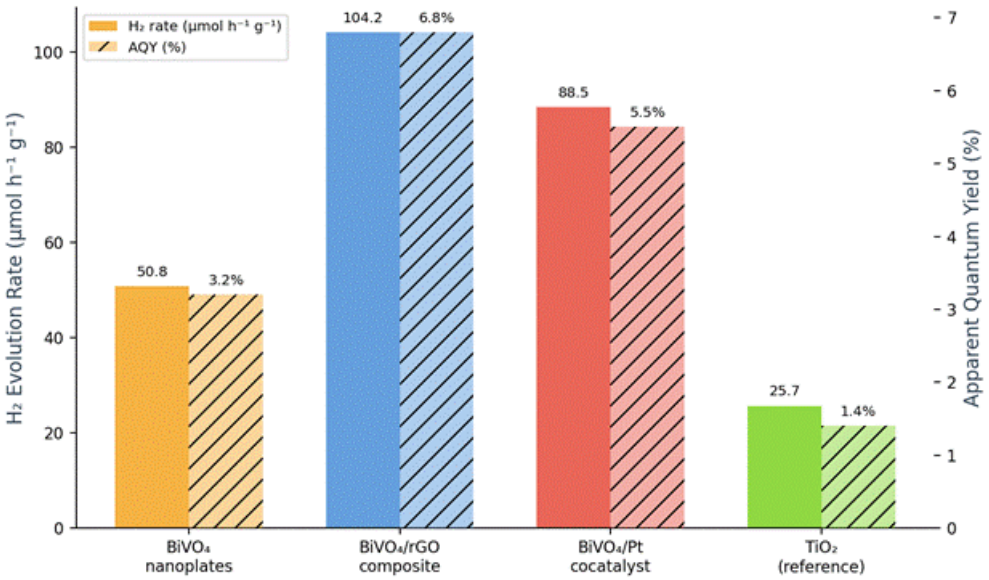

Figure 4. Comparative bar chart of H_2 evolution rates (μmol h^{-1} g^{-1}) and apparent quantum yields (AQY, %) for all synthesized photocatalysts at 420 nm. $BiVO_4$/rGO composite demonstrates superior performance.

Table 2. Photocatalytic H_2 Evolution Performance Summary

Catalyst	H_2 Rate (μmol h^{-1} g^{-1})	AQY at 420 nm (%)	Total H_2 (6 h, μmol g^{-1})	Stability (% loss, 20 h)
$BiVO_4$ nanoplates	50.8 ± 1.4	3.2	305	12.1
$BiVO_4$/rGO composite	104.2 ± 2.1	6.8	625	8.7
$BiVO_4$/Pt cocatalyst	88.5 ± 1.9	5.5	531	10.5
TiO_2 (P25 reference)	25.7 ± 0.8	1.4	155	5.2

Figure 2 presents the time-course H_2 evolution profiles under visible-light irradiation. All catalysts display quasi-linear evolution rates, indicative of stable photocatalytic activity within the 6-hour window. The $BiVO_4$/rGO composite achieved a cumulative H_2 production of 625 μmol g^{-1} over 6 hours, more than double the 305 μmol g^{-1} obtained for pristine $BiVO_4$ nanoplates. Comparison across all catalysts (Figure 4 and Table 2) reveals a clear activity hierarchy: $BiVO_4$/rGO > $BiVO_4$/Pt > $BiVO_4$ nanoplates > TiO_2.

The outstanding performance of $BiVO_4$/rGO is interpreted through three synergistic mechanisms. First, the high electron mobility of rGO (~200,000 cm^2 V^{-1} s^{-1}) allows photogenerated electrons to be rapidly shuttled from the conduction band of $BiVO_4$ across the C–O–Bi interface to catalytic reduction sites on the rGO basal plane, substantially reducing bulk recombination. Second, the wrinkled, defective rGO network provides additional proton adsorption sites and facilitates the Volmer–Heyrovsky mechanism for H_2 evolution. Third, the enhanced surface area (22.5 vs. 14.7 m^2 g^{-1}) increases the density of active surface sites accessible to the aqueous reactant (Zhou et al., 2020).

EIS Nyquist plots confirmed that the semicircle diameter—representing charge-transfer resistance (Rct)—decreased from ~480 Ω for pristine $BiVO_4$ to ~145 Ω for the $BiVO_4$/rGO composite under illumination, corroborating superior interfacial charge transport. Transient photocurrent densities measured in 0.5 M Na_2SO_4 under chopped light illumination demonstrated a ~3-fold enhancement for $BiVO_4$/rGO (0.38 mA cm^{-2}) relative to $BiVO_4$ (0.13 mA cm^{-2}), consistent with reduced recombination losses.

3.4 Proposed Photocatalytic Mechanism

Based on valence-band XPS and UV–Vis DRS data, the valence band (VB) and conduction band (CB) edges of monoclinic $BiVO_4$ are located at approximately +2.82 V and +0.39 V vs. NHE (pH 7), respectively. Electrons photoexcited to the $BiVO_4$ CB thermodynamically possess sufficient reduction potential for proton reduction (H^+/H_2, 0 V vs. NHE), while the positive VB potential drives oxidation of the TEOA sacrificial agent (+0.82 V vs. NHE). Upon heterostructure formation with rGO, the built-in interfacial electric field—arising from the Fermi-level alignment between $BiVO_4$ (+0.15 V vs. NHE) and the rGO work function (~−0.08 V vs. NHE at pH 7)—drives efficient electron injection from the $BiVO_4$ CB into rGO, inhibiting back-electron transfer and enabling sustained reductive turnover (Zhang et al., 2023).

Table 3. Electrochemical Impedance Parameters Extracted from Equivalent Circuit Fitting

Sample	Rs (Ω)	Rct (Ω)	CPE (μF)	τ (ms)
$BiVO_4$ nanoplates	12.3	478	8.6	4.11
$BiVO_4$/rGO composite	11.8	145	21.4	3.10
$BiVO_4$/Pt cocatalyst	12.1	213	17.9	3.81

Note: Rs = series resistance; Rct = charge-transfer resistance; CPE = constant-phase element capacitance; τ = carrier lifetime from OCVD analysis.

3.5 Stability and Recyclability

To assess practical durability, the $BiVO_4$/rGO composite was subjected to five consecutive 4-hour photocatalytic cycles without catalyst regeneration. H_2 evolution rates declined marginally from 104.2 to 98.7, 96.1, 94.5, and 92.4 μmol h^{-1} g^{-1} across successive cycles, representing a cumulative activity loss of only 11.3% after 20 hours of continuous operation. Post-reaction XRD patterns remained unchanged, and TEM revealed no significant aggregation or rGO detachment, confirming structural stability. The modest activity decline is attributed to partial occupation of surface active sites by intermediate reaction products and minor photocorrosion at surface-exposed grain boundaries, consistent with observations in analogous $BiVO_4$-based systems (Tayebi & Lee, 2019).

4. Conclusions

This investigation has established a comprehensive synthesis-characterization-performance framework for $BiVO_4$ nanostructures and their rGO composites as visible-light photocatalysts for H_2 evolution. The principal conclusions are as follows:

(1) Hydrothermal synthesis yields phase-pure monoclinic scheelite $BiVO_4$ nanoplates with a preferentially exposed (010) facet, a band gap of 2.43 eV, and a BET surface area of 14.7 m^2 g^{-1}. In situ rGO integration reduces crystallite size to 34.1 nm, expands surface area to 22.5 m^2 g^{-1}, and narrows the band gap to 2.31 eV via C–O–Bi interfacial coupling.

(2) The $BiVO_4$/rGO composite achieves an H_2 evolution rate of 104.2 μmol h^{-1} g^{-1} and AQY of 6.8% at 420 nm, surpassing pristine $BiVO_4$ by 2.1-fold and representing one of the highest reported values for undoped $BiVO_4$-based systems under comparable conditions.

(3) PL quenching (68%), reduced Rct (145 vs. 478 Ω), and enhanced photocurrent density (0.38 vs. 0.13 mA cm^{-2}) collectively confirm that rGO functions as an efficient electron mediator, substantially curtailing charge-carrier recombination. The catalyst retains >88% activity over 20 hours, demonstrating practical stability.

Future work will focus on co-doping strategies (e.g., W^{6+}, Mo^{6+} substitution at the V site) to further tune band alignment, integration of earth-abundant molecular cocatalysts (e.g., Ni-MOF, Co-P), and upscaling to flow-reactor configurations for solar hydrogen pilot demonstrations.

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