Supporting Information

# Heating-Rate Controlled Defect Engineering in $BiVO_4$ Thin Films for Enhanced Photoelectrochemical Water Splitting

**Table S1.** Summary of recently reported strategies for improving the current density of $BiVO_4$.

| **Study / Reference** | **Synthetic Protocol** | **$BiVO_4$ Type** | **Current Density ($mA/cm^2$)** | **Electrolyte Composition** | **Key Highlights and Comparative Advantages** |
|---|---|---|---|---|---|
| Fu et al., Nanomaterials, 2024 | Spin Coating + Annealing | Pristine $BiVO_4$ | 2.94 | Borate buffer (pH 9.3) | Less control over defect location; requires high-pH buffer; lower photocurrent |
| Zhang et al., Nat. Commun., 2024 | Surface Dipole Engineering | Pristine $BiVO_4$ | 3.6 | KPi (pH 7.0) | Complex surface treatments; less scalable; stability not reported |
| Liu et al., PCCP, 2023 | DFT-Engineered Vacancy Distribution | Pristine $BiVO_4$ | 2.9 | KPi + $Na_2SO_3$ (pH 7.0) | Theoretical focus; lacks experimental validation and stability test |
| Han et al., EES, 2018 | Laser Ablation | Pristine $BiVO_4$ | 3.6 | KPi buffer (pH ~7.0) | High photocurrent but uses laser ablation, which is costly and non-scalable |
| Wu et al., Appl. Catal. B, 2018 | Multi-layer Deposition | Pristine $BiVO_4$ | 3.1 | KPi + CoPi (pH ~7.2) | Multi-layered process; moderate stability; lower control of morphology and Ov |
| This Work (2025) | Spin Coating + Controlled Heating Rate | Pristine $BiVO_4$ | 3.17 | 0.1 M $Na_2SO_4$ + 0.1 M $Na_2SO_3$ (pH ~9.26) | Scalable and simple method; optimized heating rate creates Ov without doping or cocatalysts; reduces bandgap to 2.33 eV; superior surface porosity; 4.5 h stability |

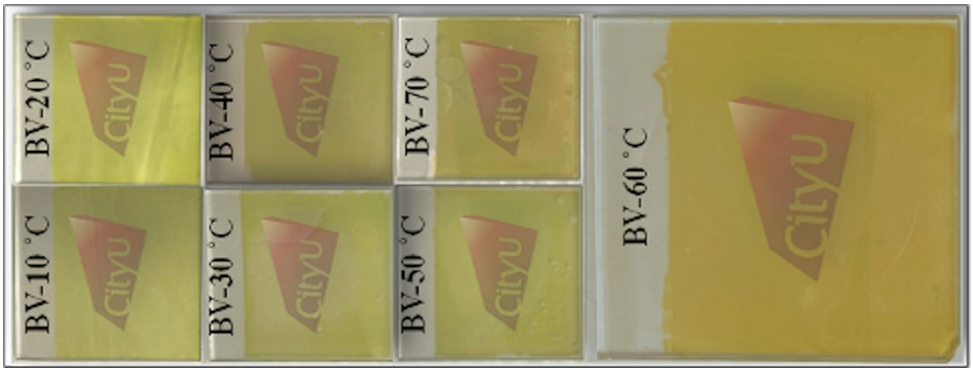


**Figure S1.** Digital photographs of as prepared samples at selected heating rates.

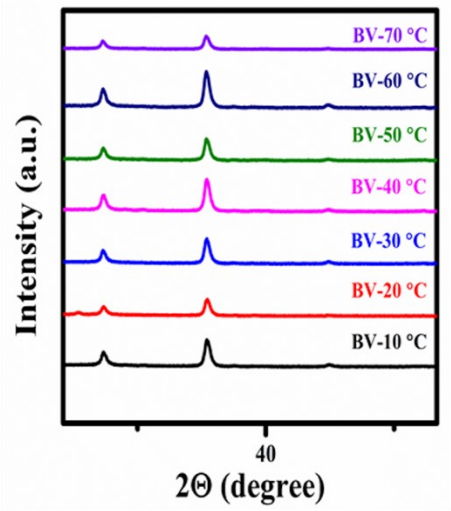


**Figure S2.** Magnification of XRD peak intensities.

| XRD Peaks | Associated planes |
|---|---|
| 18.91 | 101 |
| 28.8 | 112 |
| 30.4 | 004 |
| 37.6 | 211 |
| 42.3 | 105 |
| 46.7 | 204 |
| 53.4 | 301 |
| 54.7 | 312 |

**Table S3.** indicating XRD peaks observed in all samples and their respective planes.

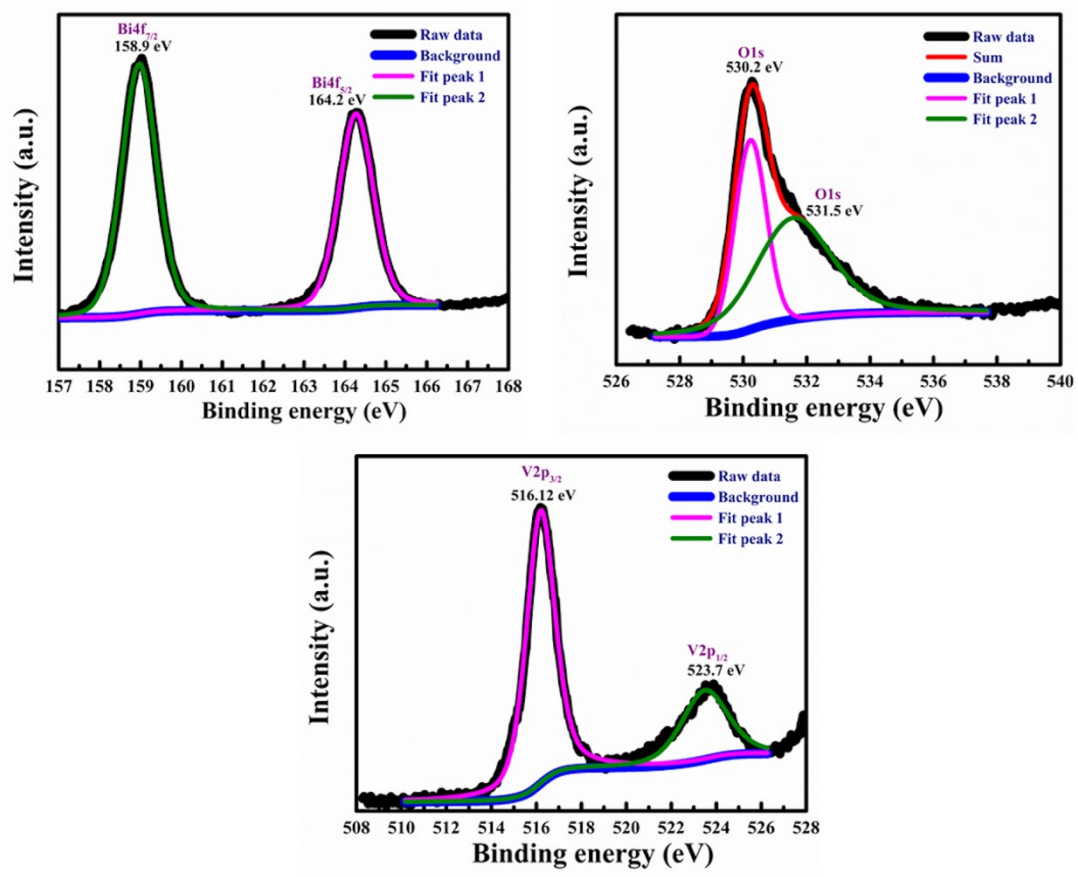


**Figure S4.** XPS peaks deconvolution for splitting bands of Bif4, O1s, and V2p (BV-60 °C), an intense peak at 531.5 eV for O1s is indicating the richness of this sample in oxygen vacancies.

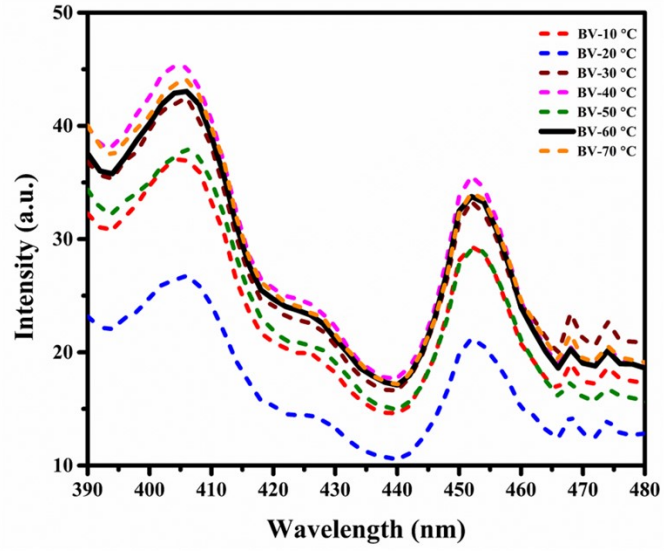


**Figure S5.** Photoluminescence (PL) spectroscopy of $BiVO_4$ films annealed at different heating rates.

**Supplementary note 1.** PL spectroscopy is a data collected by the recombination of photogenerated electrons-hole pairs. Hence if the intensity of the curve obtained is higher, the higher will be the recombination of photogenerated charges. In other words, the material will exhibit lower photoactivity, because most of the charges will recombine beforehand their participation in photocurrent generation. Figure S5 represents the PL spectra of $BiVO_4$ samples, where BV-60 °C is exhibiting charge recombination as high as BV-30 °C, BV-40 °C, and BV-70 °C. If we see I-t curves (Figure 5a), the photocurrent density of BV-60 °C is the highest among all the samples which tells that its charge generation property is excellent. If a material generates higher number of photoelectrons with a poor charge trapping property, the charge recombination curve (PL) should be as high as I-t curve among all the samples. But, here the PL spectra of BV-60 °C exhibited the charge recombination at the same rate as BV-30 °C, BV-40 °C, and BV-70 °C. Hence, oxygen vacancies rich BV-60 °C suppressed charge recombination process efficiently which resulted in achieving remarkable photocurrent density.

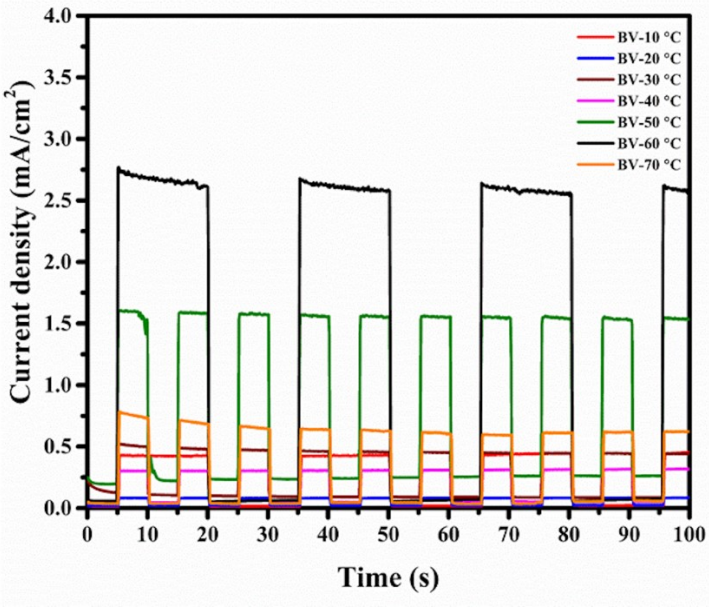


**Figure S6.** Chopped transient current density under the EE (electrode to electrolyte) illumination at 1.23 V vs. RHE.

## References


1. H. Fu, X. Chen, Y. Liu and M. Zhao, Nanomaterials, 2024, 14, 1270.
2. L. Zhang, H. Wei, T. Wu and Y. Li, Nat. Commun., 2024, 15, 1–11.
3. Y. Liu, Z. Chen, J. Zhao and Y. Wang, Phys. Chem. Chem. Phys., 2023, 25, 19324–19332.
4. H. S. Han, S. Shin, H. H. Lee and J. H. Kim, Energy Environ. Sci., 2018, 11, 1299–1306.
5. J. M. Wu, L. Zhang, D. Chen and X. Jiao, Appl. Catal. B: Environ., 2018, 221, 187–195.