

Supporting Information

From Photocorrosion to Photoactivity: Sulfite-Gated Self-Etching of BiVO₄ into Black Bi-O phase

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Supporting Figures

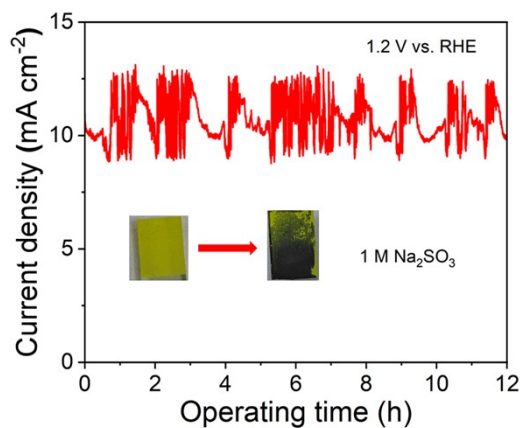


Figure S1. Chronoamperometric behavior of BiVO₄ at 1.2 V vs. RHE under otherwise identical conditions, showing visible blackening after treatment.

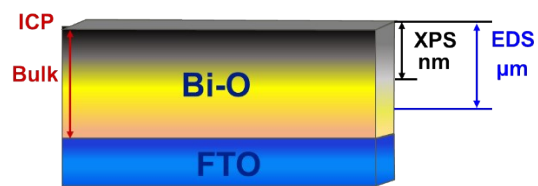


Figure S2. The EDS, XPS and ICP analysis of Bi-O on FTO.

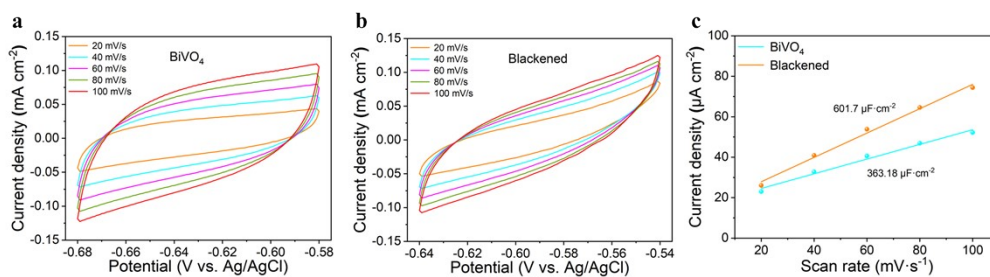


Figure S3. The calculated C_{dl} value of BiVO_4 and Blackened.

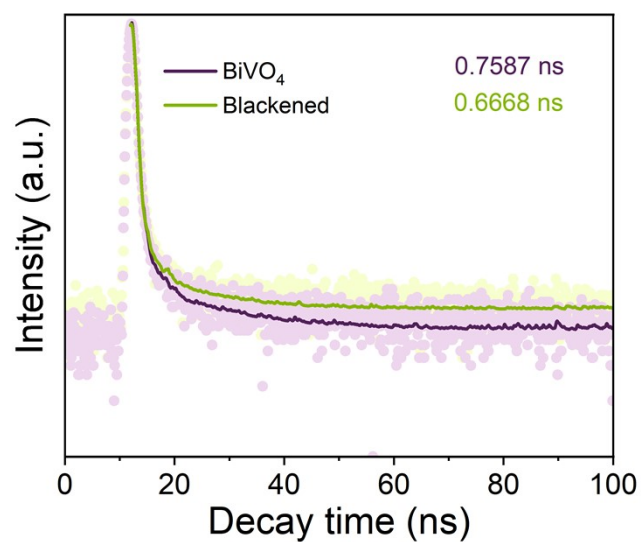


Figure S4. TRPL decay curves of BiVO₄ and Blackened.

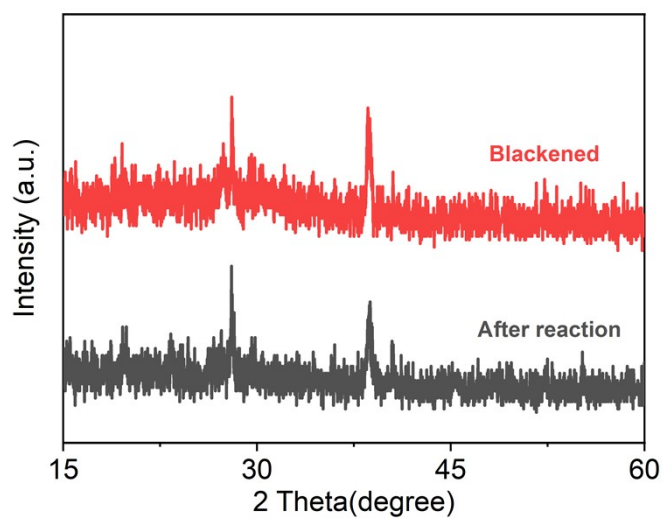


Figure S5. Post-reaction XRD characterization of the Blackened after the long-term stability test.

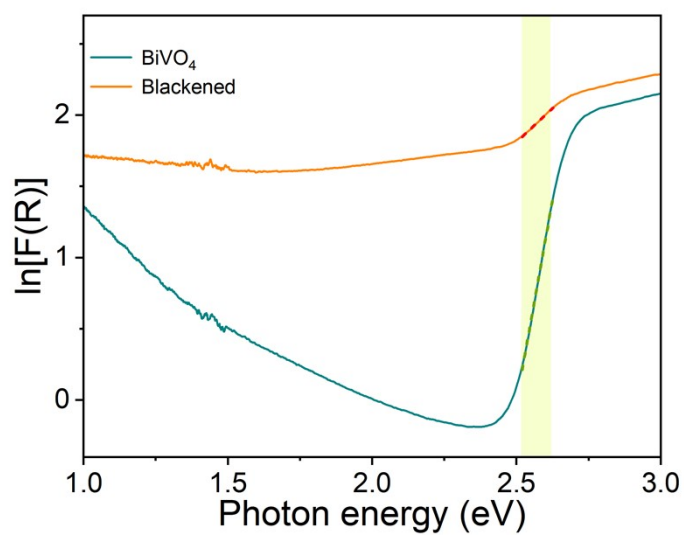


Figure S6. Linear fitting of $\ln[F(R)]$ versus photon energy for estimating the Urbach energy of BiVO_4 and Blackened.

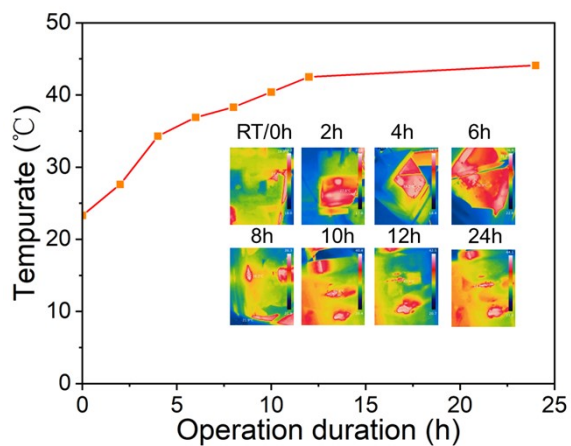


Figure S7. Temperature evolution of the blackened electrode under filtered illumination excluding wavelengths above 575 nm. A similar temperature increase is observed relative to the original irradiation condition.

Supporting Tables

Table S1. Quantitative comparison of Bi and V before and after reconstruction based on XPS, EDS, and ICP analyses.

| Sample | Methods | Bi | V | Bi:V |
|------------------------|---------|-----------------------------|-----------------------------|-------|
| BiVO ₄ | XPS | 8.32(Atomic %) | 6.23(Atomic %) | 1.34 |
| Blackened | XPS | 8.07(Atomic %) | 0.05(Atomic %) | 161.4 |
| BiVO ₄ | EDS | 7.36(Atomic %) | 7.13(Atomic %) | 1.03 |
| Blackened | EDS | 6.92(Atomic %) | 0.06(Atomic %) | 115 |
| BiVO ₄ | ICP | 6.72×10^{-4} (mol) | 7.39×10^{-4} (mol) | 0.91 |
| Blackened | ICP | 5.60×10^{-4} (mol) | 6.12×10^{-5} (mol) | 9.15 |
| Post reaction solution | ICP | 3.83×10^{-5} (mol) | 4.51×10^{-4} (mol) | 0.085 |

Table S2. Quantitative comparison of the fitted O 1s components for pristine BiVO₄ and Blackened.

| Sample | Lattice O (%) | Vacancy-related O (%) | Adsorbed O / OH (%) |
|-------------------|---------------|-----------------------|---------------------|
| BiVO ₄ | 61 | 27 | 12 |
| Blackened | 34 | 43 | 23 |

Table S3. Urbach energy analysis of BiVO₄ and Blackened.

| Sample | Fitting range (eV) | Slope of $\ln[F(R)]$ vs. (hv) | (E _U) (eV) | (R ²) |
|-------------------|--------------------|-------------------------------|------------------------|-------------------|
| BiVO ₄ | 2.52–2.62 | 11.38 | 0.088 | 0.9988 |
| Blackened | 2.52–2.62 | 1.90 | 0.525 | 0.9990 |