Supporting Information

**Insights on Z-scheme interfacial charge transfer of TiO2-NRAs/BiOI-NFs/Au-NPs nanoheterostructures and unveiling enhanced photoelectrochemical performances**

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Figure S1. The X-ray photoelectron spectroscopy (XPS) survey spectra of pristine TiO2-NRAs and TiO2-NRAs/BiOI-NFs/Au-NPs nanocomplex (a), and the high-resolution XPS spectra of (b) Ti 2p, (c) Bi 4f, (d) I 3d, (e) Au 4f, respectively.



Figure S2. Time-resolved PL (TRPL) spectra of the pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs nanoheterojunctions, respectively.



Figure S3. N2 adsorption-desorption isotherms of pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs composites.



Figure S4. (a)-(e) Cyclic voltammograms at different scan rates increasing from 20 mV/s to 100 mV/s, and (f) current density differences of pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs plotted against scan rates.

BiOI-Au-TiO2 photocurrent and EIS

Figure S5. Transient photocurrent response (a), and electrochemical impedance spectra (b) of pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs, respectively.



Figure S6. DMPO spin-trapping ESR spectra of ⋅O2- and ⋅OH under simulated solar light irradiation illustrated in (a) and (c), and in dark conditions of (b) and (d) for as-obtained pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs, respectively.

Table S1. Surface atomic ratios Ti3+/Ti4+ of Ti 2p XPS spectra for spin-orbit splitting doublets Ti 2p1/2 and Ti 2p3/2 towards to the specimens of pure TiO2-NRAs, binary TiO2-NRAs/BiOI-NFs, and ternary TiO2-NRAs/BiOI-NFs/Au-NPs, respectively.

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| --- | --- | --- | --- |
| as-prepared samples | assignment | binding energy (eV) | surface atomic ratio Ti3+/Ti4+ |
| TiO2-NRAs | Ti 2p3/2 | 459.0 | 0.906 |
| Ti3+ 2p3/2 | 458.7 |
| Ti4+ 2p3/2 | 459.1 |
| Ti 2p1/2 | 464.7 |
| Ti3+ 2p1/2 | 464.2 |
| Ti4+ 2p1/2 | 465.0 |
| TiO2-NRAs/BiOI-NFs | Ti 2p3/2 | 458.4 | 1.04 |
| Ti3+ 2p3/2 | 458.4 |
| Ti4+ 2p3/2 | 458.8 |
| Ti 2p1/2 | 464.2 |
| Ti3+ 2p1/2 | 463.9 |
| Ti4+ 2p1/2 | 464.5 |
| TiO2-NRAs/BiOI-NFs/Au-NPs | Ti 2p3/2 | 458.7 | 1.19 |
| Ti3+ 2p3/2 | 458.3 |
| Ti4+ 2p3/2 | 458.9 |
| Ti 2p1/2 | 464.4 |
| Ti3+ 2p1/2 | 463.5 |
| Ti4+ 2p1/2 | 464.4 |

Table S2. Surface Vo/(Lo + Ao) molar ratios of O 1s XPS spectra for the specimens of pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs, respectively.

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| --- | --- | --- | --- |
| As-obtained specimens | Assignment | Binding energy (eV) | Vo/(Lo + Ao) |
| pristine TiO2-NRAs | Lo | 529.7 | 0.109 |
| Vo | 531.2 |
| Ao | 532.2 |
| pure BiOI-NFs | Lo | 529.9 | 0.087 |
| Vo | 530.9 |
| Ao | 532.1 |
| BiOI-NFs/Au-NPs | Lo | 530.0 | 0.186 |
| Vo | 531.2 |
| Ao | 532.1 |
| TiO2-NRAs/BiOI-NFs | Lo | 530.1 | 0.313 |
| Vo | 531.1 |
| Ao | 532.4 |
| TiO2-NRAs/BiOI-NFs/Au-NPs | Lo | 530.3 | 0.367 |
| Vo | 531.6 |
| Ao | 532.4 |

Table S3 Fast and slow decay times along with their amplitudes and average PL lifetime (τavg) for as-obtained specimens, respectively.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample code | λex (nm) | λem (nm) | τ1 (ns) | A1/(A1+A2) (%) | τ2 (ns) | A2/(A1+A2) (%) | τavg (ns) | η (%) |
| pristine TiO2-NRAs | 375 | 396 | 4.26 | 25.7 | 0.56 | 74.3 | 3.25 | 4.3 |
| pure BiOI-NFs | 375 | 425 | 4.35 | 26.5 | 0.63 | 73.5 | 3.27 | 4.9 |
| BiOI-NFs/Au-NPs | 375 | 608 | 4.42 | 28.6 | 0.68 | 71.4 | 3.32 | 5.8 |
| TiO2-NRAs/BiOI-NFs | 375 | 639 | 4.63 | 38.3 | 0.73 | 61.7 | 3.65 | 8.9 |
| TiO2-NRAs/BiOI-NFs/Au-NPs | 375 | 659 | 4.88 | 41.5 | 0.76 | 58.5 | 4.16 | 9.9 |

Table S4 BET surface area (SBET), pore volumes (Vp), and the electrochemical double-layer capacity (Cdl) of pristine TiO2-NRAs, pure BiOI-NFs, BiOI-NFs/Au-NPs, TiO2-NRAs/BiOI-NFs, and TiO2-NRAs/BiOI-NFs/Au-NPs, respectively.

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| --- | --- | --- | --- |
| Specimens | SBET (m2﹒g-1) | Vp (cm3﹒g-1) | Cdl (μF﹒cm-2) |
| pristine TiO2-NRAs | 22.8 | 0.06 | 10.27 |
| pure BiOI-NFs | 9.8 | 0.02 | 43.31 |
| BiOI-NFs/Au-NPs | 15.5 | 0.03 | 71.19 |
| TiO2-NRAs/BiOI-NFs | 28.7 | 0.13 | 87.92 |
| TiO2-NRAs/BiOI-NFs/Au-NPs | 37.9 | 0.18 | 96.36 |