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Supporting Information

Insights into S-scheme charge transfer in α-Bi₂O₃/TiO₂-NRAs nanoheterostructures for enhanced photodegradation and biosensing applications

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Experimental Section

1 Preparation of TiO₂-NRAs/FTO substrates via hydrothermal synthesis

All reagents and solvents were procured from commercial sources and used without any further purification. Prior to the reaction, the fluorine-doped tin oxide (FTO) substrate measuring 1 cm \times 1.5 cm was thoroughly cleaned using acetone, ethanol, and deionized (DI) water. The growth of TiO₂-NRAs was achieved directly on the FTO substrate via a hydrothermal method. To initiate the process, 30 ml of DI water and 30 ml of HCl were combined, mixed, and stirred for a duration of 10 min. Subsequently, 1 ml of butyl titanate was added to the solution, followed by an additional 15 minutes of stirring. The resulting solution was then transferred into a reactor, with the clean FTO substrate positioned vertically on the inner wall of the reactor. The reaction was allowed to proceed for 6 h at a temperature of 150°C, after which the samples were rinsed with DI water. Finally, the samples were subjected to calcination in air at 450°C for a duration of 90 min.

2 Fabrication of pristine α -Bi₂O₃/FTO films, and binary α -Bi₂O₃/TiO₂-NRAs nanoheterojunctions

The above-prepared TiO₂-NRAs created on the FTO substrate were electrochemically deposited with α -Bi₂O₃ NPs. Scheme S1 illustrates the synthetic procedures for the sample preparation of pure TiO2-NRAs/FTO, pristine a-Bi₂O₃/FTO films, and binary α -Bi₂O₃/TiO₂-NRAs nanoheterojunctions. Electrochemical deposition of α -Bi₂O₃ NPs films was carried out in a three-electrode cell equipped with a Ag/AgCl electrode as the reference electrode, a pristine TiO₂-NRAs/FTO as the working electrode, and Pt plate as the counter electrode. The deposition solution of α -Bi₂O₃ NPs films was composed of a bismuth oxide with a concentration of 10^{-3} mol/L, perchloric acid (HClO₄) with a concentration of 1 mol/L, and distilled water. The electrolyte solution was stirred constantly by a magnetic stirrer throughout the electrodeposition process. A constant potential of -0.9 V was applied vs the Ag/AgCl reference electrode using a potentiostatic model of the CHI660E electrochemistry workstation (CH Instruments Co. Ltd., China). The constant potential was applied for different duration times of 10 min, 15 min, 20 min, and 40 min severally denoted as BT-10, BT-15, BT-20, and BT-40, in order to deposite α -Bi₂O₃ NPs films for different thicknesses. At last, as the reference for optical properties and PEC performances, the pristine α -Bi₂O₃/FTO films was prepared by three-electrode electrochemical depositing route with duration time 20 min, and the other experimental parameters were set same as described above.

After we rinsed the as-prepared specimens with deionized water, we dried them with a nitrogen gas flow. To facilitate the generation of intrinsic defects and the expected crystalline phases, we annealed the as-obtained specimens in a furnace in dry air. The annealing temperature was 750 °C, and the time was 30 min. The heating rate was 10 °C/min, and the cooling rate was 10 °C/min. The choice of the annealing temperature was deliberate to avoid the transformation of the crystal structure of α -Bi₂O₃ into β -Bi₂O₃ or γ -Bi₂O₃ during the annealing process (annealing temperature < 750 °C).^[15]



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Scheme S1 Synthetic procedures for preparation of pristine α -Bi₂O₃/FTO films (a), pure TiO₂-NRAs/FTO (b), and dual α -Bi₂O₃/TiO₂-NRAs heterostructures nanohybrids (c), respectively.

3 Characterization

The top view and cross-sectional morphologies of the as-prepared heterostructure nanocomposites were investigated using scanning electron microscopy (SEM, Hitachi S4200) operating at accelerating voltage of 15.0 kV. By using the UV-vis spectrophotometer (UV-1800, Shimadzu), the UV-Visible diffuse reflectance spectrometry (UV-vis DRS) measurements were performed in air at room temperature. High-resolution transmission electron microscopy (HRTEM) observation was carried out on a transmission electron microscope (TEM, JEOL JEM-2100) working at 200 kV. The phase purity and crystal structure of the prepared samples were characterized by an X-ray diffractometer (XRD, Shimadzu XRD-600) using Cu k α radiation (λ = 15.418 nm) as the X-ray source and employing a scanning rate of 0.02° s⁻¹ in the 20 range of 20° - 80°. The oxidation states of Bi, Ti, and O elements at the α -Bi₂O₃/TiO₂-NRAs nanoheterostructure surface were examined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Scientific Ltd.). The X-ray source was the Al anode emitting the Ka (1486.6 eV) radiation of 150 W. Ultraphotoelectron spectroscopy (UPS) by Thermo Fisher Scientific ESCALAB 250 XI system with a He I source with excitation energy of 21.22 eV, and the work function was determined from the UPS spectra by subtracting their width (that is, the energy difference between the analyzer Fermi level and the high binding energy cut-off), from the He I excitation energy.

A Ti: sapphire femtosecond (fs) laser system (Spectra-Physics) was used to excite the NTRT-PL. The excitation laser beams with wavelengths centered at 266 nm, is acquired accordingly by sum frequency of 800 nm and 400 nm $(400^{-1} + 800^{-1} = 266^{-1})$ femtosecond laser beams through a BBO (beta-BaB2O4, barium metaborate) crystal, with pulse duration of 130 fs, repetition rate of 1 kHz and spot size of 1 mm. The PL emission is collected by a spectrometer (Bruker Optics 250 IS/SM) coupled with an intensified charge-coupled device (CCD) detector (IStar 740, Andor). Nanosecond time-resolved experiments were carried out by adjusting the delay time of the CCD shutter. A laser pulse gave an external trigger signal to open the 100-ms and 0.5-ns temporal gates of the intensified CCD through a synchronization/delay generator (SDG) and digital delay/pulse generator (DG 535) then the transient PL spectra at different decay times could then be recorded by the CCD detector. Scheme S2 gives a schematic diagram of the experimental setup. The TRPL data were measured in a home-built single photon counting system, in which a picosecond pulsed diode laser $(\lambda_{ex}=375$ nm, PicoQuant, LDH-P-C-375) with the pulse FWHM less than 40 ps was installed as the excitation source. The signals collected at the PL emission of Vo defect states (λ_{em} = 2.9 eV) for TiO₂-NTAs were dispersed with a grating spectrometer, detected by a high-speed photomultiplier tube, and then correlated using a single photon counting card.



Scheme S2 Experiment setup of nanosecond time-resolved transient PL (NTRT-PL)

measurements.

The fs-TAS setup typically includes a femtosecond Ti laser, an optical parametric amplifier (OPA), and a transient absorption spectrometer. Figure 3 gives a schematic diagram of the fs-TAs experimental setup. The Ti laser generates femtosecond laser pulses at a central wavelength of 800 nm, which are then split into two beams of differing intensities using a beam splitter. The more intense beam is directed through a chopper and further processed by the OPA to create a short-wavelength pump pulse. This pump pulse excites the sample from its ground state to an excited state. The weaker beam, acting as the probe pulse, passes through an optical delay line and interacts with a sapphire crystal, producing a broadband white light continuum. This probe pulse is used to monitor changes in the sample by overlapping with the pump pulse at the same spatial point on the sample surface. After passing through the sample, the probe pulse is directed to a detector, while the pump pulse is blocked by a beam stopper. The optical delay line adjusts the time delay between the pump and probe pulses, allowing the investigation of dynamic processes within the sample at various time intervals. By comparing the absorption of the probe pulse with and without the pump pulse, the transient absorption spectra can be obtained, reflecting the changes in the excited state populations over time. Through this, the relaxation dynamics of charge carriers and their return to the ground state can be accurately tracked.



Scheme S3 Experiment setup of femtosecond transient absorption spectroscopy (fs-TAs)

measurements.

The PEC-related performance tests were performed using an CHI660E electrochemical workstation under AM 1.5G illumination provided by a solar simulator (SS150A, ZOLIX, 100 mW/cm²), including the photocurrent density versus testing time curve (Amperometric I-t curve), and electrochemical impedance spectra (EIS). The Mott-Schottky plots of samples were performed in a 0.5 M Na₂SO₄ electrolyte to assess the flat band potential of the as-prepared samples, which was carried out at a frequency of 1 kHz. Unless specified otherwise, all normal hydrogen electrode (E_{NHE}) potentials in this study were deduced from the potentials obtained by the Ag/AgCl electrode based on the following equation: $E_{NHE} = E_{Ag/AgCl} + 0.1976V$, and a Pt-plate counter electrode were employed during the measurements.

4 Photodegradation of methyl orange (MO) and PEC biosensing of glutathione (GSH) measurements

Moreover, the photocatalytic activities of the α -Bi₂O₃/TiO₂-NRAs type-II heterostructure films compared with pristine TiO₂-NRAs were investigated using the

photodegradation of MO under a standard solar simulator (AM 1.5) powered by 300 W tungsten halogen lamp to provide UV-Visible light irradiation. All chemicals were of analytical grade and aqueous solutions were prepared with ultrapure water (Milli-Q, Millipore), MO (5 mg) was dissolved in 500 mL of de-ionized water to yield a concentration of 10 mg/L. The supernatant was transferred to a quartz cuvette to measure its absorption spectrum. The catalyst-containing solution was exposed to UV-Visible irradiation for different duration at room temperature. The concentration of MO solution was checked every 0.5 h using UV-Vis spectrophotometer by monitoring the intensity variation for the characteristic absorption peak at 465 nm. For detecting the reactive species during photocatalytic degradation, the trapping experiments of active species were taken out by using 2 mM methanol aqueous solution, and 2 mM isopropanol (IPA) as holes (h⁺) and the hydroxyl radicals (·OH) scavengers, respectively. Besides, N₂-bubbling for inhibiting the superoxide radical (·O₂⁻). The photocatalytic conditions were similar to the above experiments.

PEC biosensoring performance measurements were performed with a home-built PEC system. Reduced GSH was purchased from Aladdin Chemistry Co. Ltd. Simultaneously, 0.1 mol L⁻¹ phosphate-buffered saline (PBS) was always employed as the supporting electrolyte after being deaerated with high-purity nitrogen, and the pH value of PBS was 7.0 unless indicated otherwise. Photocurrent was measured by the current-time curve experimental technique on a CHI660E electrochemical workstation with a 300 W tungsten halogen lamp light as the irradiation source (simulated sunlight irradiation). All experiments were carried out at room temperature using a conventional three electrode system with the modified TiO₂-NRAs substrates as the working electrode, a Pt plate was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The applied potential was 0 V (versus Ag/AgCl) and the detection limit was determined by the lowest value that could be clearly distinguished from the background signal (0 mol L⁻¹ of GSH).



Results and discussions

Figure S1(a)-(f) Depicts the XRD patterns of (a) pristine TONAs, (b) pure α -BO, and (c)-(f) the BT nanoheterostructured hybrids with varying α -BO electrodeposition times (10, 15, 20, and 40 min), respectively.



Figure S2(a) Depicts the UV-visible diffuse reflectance spectra, while Figure S2(b) presents the derived Tauc plots for the estimation of optical E_g for all crafted specimens, and the inset in Figure

S2(b) shows the variation curve in the E_g values of the BT nanohybrids as a function of the α -BO electrodeposition time from 10 to 40 min, respectively.



Figure S3(a)-(b) The UPS of (a) pure α -BO films, and (b) pristine TONAs, respectively.



Figure S4(a)-(e) High resolution XPS characterizations of O 1s for pristine TONAs (a), and (b)-(e) BT with different electrodeposition times 10, 15, 20, and 40 min, respectively.



Figure S5 Mott-Schottky (M-S) plots of the BT nanohybrid s with deposition times of α -BO set at

10, 15, 20, and 40 min collected at a frequency of 1 kHz, respectively.



Figure S6 Presents the TRPL spectra of the pristine TONAs and the BT nanohybrid structures,

with deposition times of α -BO set at 10, 15, 20, and 40 min.



Figure S7 (a)-(b) Transient photocurrent response (a) and (b) EIS of pristine TONAs, and BT

binary nanoheterojunctions with various α-BONPs deposition times 10, 15, 20, and 40 min,





Figure S8(a)-(d) DMPO spin-trapping ESR spectra of $\cdot O_2^-$ and $\cdot OH$ under simulated solar light irradiation illustrated in (a) and (c), and in dark conditions of (b) and (d) for as-obtained pristine TONAs, and BT binary nanoheterojunctions with various α -BONPs deposition times 10, 15, 20,

and 40 min, respectively.



Figure S9 Calibration curve for MO at various concentrations.



Figure S10(a)-(b) (a) Under simulated solar light irradiation, the time-dependent photocurrent performance of the BT-20 sample was evaluated in a 0.1 M PBS solution containing 400 μM GSH at a voltage of 0 V (relative to Ag/AgCl) after 26 cycles of irradiation. (b) The time-dependent photocurrent performance of the BT-20 sample was also assessed after being stored in a refrigerator for 7 days, following the same 26 cycles of irradiation.

Table S1 The molar ratios of surface $V_o/(L_o + V_o)$ and the main peak positions (MPP) of the O 1s

specimens	assignment	hinding energy (eV)	MPD (eV)	$V_o/(L_o + V_o)$
	assignment	omaing energy (ev)		(%)
pristine TONAs	L _o	529.3	529.5	13.1
	Vo	530.9	527.5	13.1
BT-10	L _o	529.5	52 0 C	10.2
	V _o	531.1	529.6	19.3
BT-15	L _o	529.6	520.7	27.5
	Vo	531.0	529.7	27.5
BT-20	Lo	529.7	529.7	
	V _o	531.1	329.8	31.3

XPS spectra for the synthesized unary and binary specimens.

	Lo	529.5			
BT-40			529.7	28.7	
	Vo	530.8			

Table S2 The density of donor carriers (N_d), and flat band potential (E_{fb}) for the BT nanocomplex

sample	N_d (cm ⁻³)	E _{fb} (vs. Ag/AgCl)
BT-10	9.7×10 ¹⁷	-0.681
BT-15	2.8×10 ¹⁸	-0.709
BT-20	7.3×10 ¹⁸	-0.755
BT-40	5.5×10 ¹⁸	-0.727

with deposition times of α -BO set at 10, 15, 20, and 40 min, respectively.

Table S3 Presents the fast and slow decay times, their respective amplitudes, and the average

Sample code	λ_{ex} (nm)	λ_{em}	τ_1	A ₁ /(A ₁ +A ₂)	τ_2	$A_2/(A_1+A_2)$	τ_{avg}	η
		(nm)	(ns)	(%)	(ns)	(%)	(ns)	(%)
pristine TONAs	375	530	4.16	25.3	0.63	74.7	3.07	4.91
BT-10	375	630	4.39	26.9	0.61	73.1	3.42	5.14
BT-15	375	630	4.45	28.9	0.65	71.1	3.49	5.65
BT-20	375	630	4.79	40.6	0.75	59.4	4.03	9.63
BT-40	375	630	4.59	38.9	0.76	61.1	3.79	8.95

photoluminescence lifetime (τ_{avg}) for the obtained samples.