Photocatalysis

Enhancing Mo:BiVO₄ Solar Water Splitting with Patterned Au Nanospheres by Plasmon-Induced Energy Transfer

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Plasmonic metal nanostructures have been extensively investigated to improve the performance of metal oxide photoanodes for photoelectrochemical (PEC) solar water splitting cells. Most of these studies have focused on the effects of those metal nanostructures on enhancing light absorption and enabling direct energy transfer via hot electrons. However, several recent studies have shown that plasmonic metal nanostructures can improve the PEC performance of metal oxide photoanodes via another mechanism known as plasmon-induced resonant energy transfer (PIRET). However, this PIRET effect has not yet been tested for the molybdenum-doped bismuth vanadium oxide (Mo:BiVO₄), regarded as one of the best metal oxide photoanode candidates. Here, this study constructs a hybrid Au nanosphere/Mo:BiVO4 photoanode interwoven in a hexagonal pattern to investigate the PIRET effect on the PEC performance of Mo:BiVO₄. This study finds that the Au nanosphere array not only increases light absorption of the photoanode as expected, but also improves both its charge transport and charge transfer efficiencies via PIRET, as confirmed by time-correlated single photon counting and transient absorption studies. As a result, incorporating the Au nanosphere array increases the photocurrent density of Mo:BiVO₄ at 1.23 V versus RHE by ≈2.2-fold (2.83 mA cm⁻²).

1. Introduction

Splitting water into hydrogen and oxygen using a photoelectrochemical (PEC) cell is a potential pathway for solar energy conversion and storage.^[1] The broad adoption of such

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injection from plasmonic metal nanoparticles to the not electronis band of neighboring metal oxides, and it requires direct contact between metal and metal oxides.^[9] PIRET was recently proposed by several pioneering studies.^[9,21] PIRET utilizes the nonradiative dipole–dipole coupling between metals and metal oxides to

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PEC cells demands the development of stable, economical, and efficient photoanodes. Stable, earth-abundant metal oxides such as TiO₂, WO₃, Fe₂O₃, and BiVO₄ are popular photoanode candidates.^[2,3] However, these metal oxide photoanodes exhibit poor efficiency because they cannot achieve simultaneously high light absorption, charge separation, and charge transfer efficiencies.^[4-6] One common strategy for improving these metal oxide photoanodes is to decorate them with various plasmonic metals, such as metal nanoparticles or nanorods, to introduce nearfield localized surface plasmon resonance (LSPR) and/or surface plasmon polaritons (SPP).^[7-18] Many studies on these plasmonic metal nanostructures have focused on the light absorption enhancement effect from LSPR and SPP.^[9,19-26] In addition, LSPR can improve the performance of metal oxide photoanodes through plasmonic energy transfer through two mechanisms: direct electron transfer (DET) and plasmon-induced resonant energy transfer (PIRET).^[9,21] DET refers to the hot-electrons

generate electron-hole pairs in metal oxides. In other words, the strongly localized electromagnetic field of LSPR of the plasmonic metal excites an electron-hole pair in metal oxides without emitting a photon.^[9] The efficiency of PIRET is higher when there is more overlap between the metal oxide bandgap and the LSPR resonance band, and the distance between plasmonic metal and metal oxides is smaller.^[9] One recent study successfully implemented plasmonic gold nanoholes to improve both light absorption and energy transfer processes for hematite nanorod photoanodes through PIRET.^[23] However, in comparison to hematite, molybdenum-doped bismuth vanadium oxide, Mo:BiVO₄, (hereafter, BVO) was shown to have better PEC performance as photoanodes.^[6,14,15] Hence, it is of great interests to investigate the potential of using a highly ordered plasmonic Au metal pattern array to enhance the performance of BVO-based photoanode by employing the PIRET effect. We choose the hexagonal pattern because it is the densest way to arrange the plasmonic metals. In addition, the equal sides of a standard hexagonal maximize the interface between Au and BVO. Meanwhile, the Au arrays with the hexagonal pattern can exhibit much favorable plasmoninduced resonance for the BVO water splitting at the visible region, comparing to them with square patterns.^[26]

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In this study, we investigate the potential to enhance the PEC performance of BVO-based photoanodes with plasmonic Au nanostructures through both light absorption enhancement and plasmon-enhanced energy transfer. Plasmonic Au nanostructures are consisted of Au nanospheres in a hexagonal pattern, and the size and pitch of the Au nanospheres are designed to generate hot spots in between where BVO is placed. Those plasmonic hot spots enhance the solar light absorption of BVO over a broad ultraviolet-visible (UV-vis) spectral range. Additionally, the patterned Au nanospheres enhance both its charge transport and charge transfer efficiencies. The time-correlated single photon counting and transient absorption studies show that the presence of the Au nanosphere array increases the characteristic lifetimes of both electrons and holes, an indication of PIRET. As a result, incorporating the Au nanosphere array increases the photocurrent density of Mo:BiVO₄ at 1.23 V versus RHE (reversible hydrogen electrode) by ≈2.2-fold, reaching \approx 2.83 mA cm⁻². This Au–BVO photoanode is comparable with the state-of-the-art plasmonic-metal-incorporated metal oxide photoanodes (\approx 1.4 mA cm⁻² for BiVO₄ coupled with Au nanoparticles and ≈ 5.1 mA cm⁻² for nanoporous BiVO₄ with Au nanoparticles in sulfate electrolyte, $^{[11-14]} \approx 1.2 \text{ mA cm}^{-2}$ for Fe₂O₃ with Au nanoparticles or Au nanoholes, $^{[16,23]} \approx 1.5 \text{ mA cm}^{-2}$ for ZnO with Au nanoparticles,^[17] and \approx 2.7 mA cm⁻² for rutile TiO₂ nanorods with sputtured Au nanparticles^[28]).

2. Results and Discussion

2.1. Fabrication and Characterization

The fabrication process of the hexagonal-patterned Au–BVO photoanode is schematically illustrated in **Figure** 1a. First, we used UV nanoimprinting lithography to prepare a polyurethane acrylate (PUA) polymer mold with hexagonal-patterned pillars. The pillar mold was manually stamped onto a polymethyl methacrylate (PMMA)-coated fluorine doped tin oxide (FTO)

glass and subsequently peeled off. This process creates hexagonal-patterned nanoholes in the PMMA. The PMMA residues at the bottom of the nanoholes were removed via a brief oxygen plasma treatment to expose the FTO substrate underneath. Then, Au was electrochemically deposited inside the PMMA nanoholes (Figure S1, Supporting Information). After removing the PMMA and thermally annealing the substrate, the FTO glass was left with hexagonal-patterned Au nanospheres (Figure 1b). BVO was deposited on top of the Au/FTO by spin-coating followed by thermal annealing. The morphologies of the Au-BVO photoanodes are shown in Figure 1c,d. The BVO film (≈220 nm) was located between the Au nanospheres and the top surface of BVO was not covered by Au because of the weak affinity between the Au nanostructures and the BVO precursor.^[27] The fabricated photoanodes show no obvious changes in the crystallinity and chemical composition of BVO according to their X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) (Figure S2, Supporting Information). The diameter of the Au nanospheres could be tuned from 200 to 390 nm by changing the deposition time (30 to 180 s, respectively; Figure S3, Supporting Information). The pitch between the Au nanospheres was fixed to be 520 nm. Unless otherwise specified, we used the configuration with an Au nanoparticle diameter of 260 nm and a pitch of 520 nm for most of the PEC performance characterization described below. Due to our configuration of Au nanospheres, the hot-electron transfer effect could be negligible since it was claimed that plasmonic hot electrons can be generated in the spherical Au nanoparticles with the size of 10-20 nm, and the plasmonic light absorption was diminished by increasing the diameter of Au nanoparticles over 80 nm.^[7,9,19,25]

2.2. PEC Performance of Au-BVO Photoanodes

The PEC water oxidation performance of the Au-BVO and BVO photoanodes was characterized using linear sweep voltammetry (LSV) and wavelength-dependent external quantum efficiency (EQE) (i.e., incident photo-to-current conversion efficiency (IPCE)). These measurements were carried out in a three-electrode configuration with an Ag/AgCl reference electrode and a Pt wire counter electrode in a 0.5 м phosphate buffer electrolyte (pH 7.4) under front-side illumination. The LSV was carried out under the simulated 1 sun AM 1.5 G illumination (Figure 2a). Before comparing BVO and Au-BVO, we first determined the optimal values for the BVO film thickness and Au nanosphere diameter. We varied the BVO thickness from ≈100 to ≈350 nm (Figure S4, Supporting Information) and identified the optimal BVO thickness to be ≈220 nm for both BVO and Au-BVO photoanodes (Figure S5a-c, Supporting Information). We also changed the Au nanosphere diameters from 200 to 390 nm (Figure S3, Supporting Information) while fixing the pitch distance at 520 nm and found that the optimal diameter is ≈260 nm (Figure S5d, Supporting Information). Under these optimized conditions, the Au-BVO photoanode achieved a current density of 2.83 mA cm⁻² at 1.23 V (versus RHE), which is ≈2.2 times higher than that of the bare BVO photoanode (1.29 mA cm⁻²). The EQE spectra in Figure 2b show that the Au-BVO photoanode exhibited consistently higher EQE





Figure 1. Fabrication of the BVO photoanode incorporated with an Au nanosphere patterned array. a) Schematic illustration of the fabrication process for the photoanode incorporated with an Au nanosphere patterned array and b) SEM top-view image of the highly ordered Au nanosphere patterned array. c) SEM top-view image and d) SEM cross-sectional image after FIB milling the photoanode with the highly ordered Au nanosphere patterned array (52° tilt).

values than the bare BVO photoanode over the entire tested wavelength range (350–700 nm). The inset of Figure 2b shows that there is a significant EQE enhancement in the range of

 \approx 500–700 nm. To understand the effects of Au nanospheres on the EQE (EQE = $\eta_{abs} \times \eta_{transport} \times \eta_{transfer}$), we discuss the effect of Au on the light absorption (or harvesting) efficiency



Figure 2. Photoelectrochemical performance of the photoanodes. a) Current density versus potential curves in the dark or under AM 1.5 G 1 sun illumination with and without hole scavenger and b) external quantum efficiency (EQE) spectra of Au–BVO and BVO photoanodes in aqueous phosphate buffer (pH 7.4). (Inset figure in (b)) EQE spectra of the samples in the range of 500–700 nm. All measurements were conducted using a three-electrode configuration with an Ag/AgCl reference electrode and a Pt wire counter electrode.





Figure 3. Optical properties of the Au nanosphere patterned array and photoanodes. a) Experimentally characterized and simulated UV–vis absorptance spectra of the Au–BVO and BVO photoanodes. b) UV–vis absorbance spectrum and simulated LSPR of the Au nanosphere patterned array deposited on FTO. c) Simulated numerical rigorous coupled wave analysis field distribution ($|E|^2$) on the plane across the centers of Au nanosphere patterned array at a wavelength of 500 nm. Here, the geometry and size values of the Au nanosphere array for the simulation correspond with the experimentally measured values shown in Figure 1c of the Au nanosphere array with a diameter of 260 nm and BVO with a thickness of 220 nm.

 (η_{abs}) , efficiency of the charge transport to the BVO–electrolyte interface $(\eta_{transport})$, and the interfacial charge transfer (or surface catalytic reaction) efficiency $(\eta_{transfer})$, respectively below.

2.3. Effect of Au Nanospheres on the Light Absorption Efficiency

Figure 3a shows the measured (solid lines) and calculated (dashed lines) absorptance (i.e., light absorption efficiency η_{abs}) for bare BVO and Au-BVO photoanodes. The measured absorptance (A) was obtained by determining the UV-vis diffuse reflectance (R) and diffuse transmittance (T) spectra (A = 100% - R - T; Figure S6, Supporting Information).^[34] The simulated absorptance (A) was calculated with the numerical rigorous coupled wave analysis using the experimental geometry for Au-BVO in Figure 1c. Here, the oscillation in the simulated curves over 500 nm wavelength could be a numerical artifact. There is a weak absorption of Au-BVO at 650 nm in the experimental data, which is absent in the simulation. This difference comes from the difference in our Au configuration. The simulated curve shows the normalized absorption crosssection of a single Au sphere to identify the surface plasmon resonance frequency. However, the experimental result was obtained for the Au nanosphere pattern arrays, comprised of numerous Au nanospheres, which provides additional plasmonic coupling or scattering effect and contributes to the weak absorption at 650 nm. Both the experimental and calculated results show that the Au-BVO photoanode has a higher absorptance than the BVO photoanode over the entire wavelength range tested. Since Au nanospheres do not change the bandgap of BVO (2.4 eV, 517 nm) according to the plot of the transformed Kubelka-Munk function (Figure S7, Supporting Information), such enhancement is attributed to the plasmonic effects of the Au nanosphere array. This enhancement can be seen in Figure 3a, which shows that the absorptance of Au-BVO photoanode at 500-700 nm matches well with absorbance of the Au nanosphere array on FTO (Figure 3b).

For the calculated absorptance of Au–BVO, we subtracted the contribution of the Au nanospheres from that of Au–BVO to obtain the real absorptance of BVO in Au–BVO (blue dashed line in Figure 3a). Below 517 nm (EQE onset of BVO in Figure 2b), the simulated absorptance spectra of Au–BVO (without Au) and bare BVO photoanodes are actually similar. Since the surface coverage of BVO is \approx 70% due to the presence of Au nanospheres (Figure 1c), this enhanced light absorptance per unit volume of the BVO in Au–BVO is caused by the LSPRs, a consequence that BVO is located at sites with a strong electric field gradient formed by the Au nanospheres (Figure 3c).

2.4. Charge Separation and Transfer Efficiencies

To gain more insights into the EQE (= $\eta_{\rm abs}$ imes $\eta_{\rm transport}$ imes η_{transfer}) enhancement from Au nanospheres in Figure 2b, we calculated the internal quantum efficiency (IQE = EQE (λ) / Absorptance (λ); Figure S8, Supporting Information). The calculated IQE spectrum of Au subtracted Au-BVO (without Au) shows significantly higher efficiency (over 80%), compared to that of BVO (40-50%). Further, we carried out electrochemical impedance spectroscopy (EIS) measurements. The EIS Nyquist plots and extracted parameters are shown in Figure 4a and Table 1, respectively. The presence of Au nanospheres noticeably reduces the charge extraction resistance from the BVO to the FTO substrate (R_{CT1}) from 65.8 to 26.2 Ω , and the combined resistance of charge transport in BVO and charge transfer the BVO/electrolyte interface (R_{CT2}) is reduced from 2336 to 988 Ω . The decreased R_{CT1} implies that the Au nanosphere array provides an efficient pathway for charge extraction from BVO to FTO with lower interfacial charge recombination.^[29] The reduction of R_{CT2} indicates that the overall charge recombination within BVO is greatly reduced.

We then used the hole scavenger method (Figure 2a; Figure S9, Supporting Information)^[30–33] to extract the charge transport (or charge separation) efficiency ($\eta_{\text{transport}}$) and the charge transfer (or surface catalytic reaction) efficiency (η_{transfer}).^[34,35] Here, the photocurrent density values at 1.23 V (vs RHE) within the hole scavenger are 4.64 mA cm⁻² for Au–BVO and 2.71 mA cm⁻² for BVO. Both extracted $\eta_{\text{transport}}$ and η_{transfer} efficiencies for Au–BVO are higher than those

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Figure 4. Photoelectrochemical and electrochemical characteristics of the photoanodes. a) Electrochemical impedance spectroscopy (EIS) Nyquist plots in aqueous phosphate buffer (pH 7.4). b) Charge transport efficiency and c) charge transfer efficiency. Here, the charge transport efficiency was obtained using $\eta_{\text{transport}} = J_{\text{scavenger}}/J_{\text{abs}}$, and the charge transfer efficiency was obtained using $\eta_{\text{transfer}} = J_{\text{water}}/J_{\text{scavenger}}/J_{\text{abs}}$ is the absorbed maximum photocurrent density from the light absorptance of each sample. d) CV scan with a scan rate of 10 mV s⁻¹ over 1.7 V (versus RHE) in 0.5 M potassium phosphate electrolyte (pH 7.4) in the dark.

of BVO (Figure 4b,c). First, the superior charge transport $\eta_{\text{transport}}$ in Au–BVO is confirmed by comparing the *I*–V curves measured by front and back illumination (hereafter, J_{Front} and J_{Back}, respectively). As shown in Figure S10 (Supporting Information), $J_{\rm Front}$ (1.29 mA cm⁻²) is lower than $J_{\rm Back}$ (1.51 mA cm⁻²) for BVO at 1.23 V (versus RHE), because the poor charge transport property of BVO gives rise to the more efficient collection of the carriers generated near the FTO. By contrast, for Au-BVO, $J_{\rm Front}$ (2.83 mA cm⁻²) is higher than J_{Back} (2.57 mA cm⁻²). This result indicates that carriers generated far away from the FTO are effectively collected by the Au nanospheres.^[35-37] Second, the improved charge transfer efficiency η_{transfer} in Au–BVO is supported by the dark cyclic voltammetry (CV) measurement (Figure 4d and Figure S11, Supporting Information). For the CV measurements, we tested the Au–BVO and BVO electrodes with a thin BVO layer (≈30 nm thick) to reduce the effects from difference between the charge transport properties of BVO and Au-BVO. The CV curves in Figure 4d indicate that the Au-BVO electrode exhibits a lower

 Table 1. EIS Nyquist plot results of bare BVO and Au-BVO photoanodes. Simulated parameters from EIS Nyquist plots of the photoanodes in Figure 4b using Z-view software.

	R _s [Ω]	R_{ct1} [Ω]	R _{ct2} [Ω]
BVO	75.66	65.8	2336
Au–BVO	61.54	26.2	988

overpotential by ≈ 0.1 V and a higher current density value than the BVO electrode. This enhancement due to Au is similar to the improvement in the oxygen evolution reaction kinetics that has been observed for some other metal oxides.^[38–41]

2.5. Charge Carrier Dynamics

To better understand the effects of Au nanospheres on the enhancement of the charge transport and charge transfer efficiencies, we further investigated the charge carrier dynamics by conducting low-temperature time-correlated single photon counting (TCSPC) and transient absorbance (TA) decay profile studies. TCSPC characterization was conducted at 20 K to reduce interference from the lattice oscillation and the defect states in metal oxides.^[42,43] The measured PL decay curves (Figure 5a) were fitted by a biexponential function to capture the initial fast decay and the subsequent slow delay. The fitted parameters for the Au-BVO and BVO photoanodes are listed in Figure 5c. The fast decay component is attributed to the electron trapping into the near-conduction-band-edge states of BVO, and its time constant (τ_1) is similar for both BVO (0.30 ns) and Au-BVO (0.32 ns) photoanodes. The slow component originates from the electron-hole recombination,[44,45] and its time constant (τ_2) is longer for Au–BVO (4.25 ns) than for BVO (2.69 ns). Consequently, the intensity-weighted average lifetime $\tau_{\rm ave}$ increases from 2.34 ns for BVO to 3.66 ns for Au– BVO. The longer τ_2 and τ_{ave} values for Au–BVO indicate that





Figure 5. PL and TA decay profiles. a) Photoluminescence (PL) decay profiles in time-correlated single photon counting (TCSPC) at 20 K and b) transient absorption (TA) decay profiles. For the TA profiles, detection was carried out at a wavelength of 630 nm. The TA decay lifetime of Au–BVO increases from 81 to 116 ps. c) The PL decay curves in panel (a) were fitted by a biexponential function to calculate the lifetime of the samples. The excitation and detection wavelengths were 400 nm, 526 nm (Au-BVO) and 533 nm (BVO), respectively. ^{a)}The intensity-weighted average exciton lifetime (τ_{avr}) was $f_1\tau_1 + f_2\tau_2$, where f_1 and f_2 are the fractional intensities and τ_1 and τ_2 are the lifetimes; ^{b)} χ^2 is the reduced chi-square value.

the Au nanosphere array effectively suppresses the charge recombination. The lower charge recombination was also supported by the photocurrent transient measurements (Figure S12, Supporting Information), which show that the transient time constant for Au-BVO photoanode (0.51 s) is longer than that of the BVO photoanode (0.19 s). The reduced charge recombination indicates that PIRET dominates over DET in our BVO/Au photoanode. If DET dominates over PRIET, the hot-electron injection from plasmonic metal would increase the spontaneous recombination rate in BVO due to the increased concentration of electrons.^[46–50] The reason that DET is negligible is that our Au nanospheres have a diameter of 260 nm. Such a larger diameter (in comparison to 20 nm) will decrease the hotelectron generation rate, increase plasmon decay, and increase the Schottky barrier at the interface of Au/BVO.^[51-54] Hence, the possibility for hot-electron injection is very small.

The above time-resolved photoluminescence (TRPL) characterization confirms that the electrons show longer time constants in Au-BVO. We then used time-resolved TA measurements to investigate the transfer dynamics of holes since the photogenerated hole trapping and charge relaxation occur within few-tens picosecond scale.^[44] For the TA measurement, the photoanodes were pumped at 515 \pm 10 nm because the wavelength of 515 nm overlaps the absorptance range of BVO (<517 nm) and the LSPR range of Au nanosphere arrays (505-525 nm, estimated from the absorbance spectra and the simulated LSPR spectrum presented in Figure 3b. The TA signals were probed at 630 nm because the absorption at 630 nm is mainly attributed to the surface-trapped holes.^[45] Figure 5b shows the time-resolved TA profiles for BVO and Au-BVO fitted with a single-exponential function. The fitted decay time constant for Au-BVO is 116 ps, longer than that of BVO (81 ps). Furthermore, the long-lived hole transfer in deeper trap states was investigated within much longer time domain up to nearmillisecond scale, i.e., ≈0.5 ms, pumped at 400 nm and proved at 633 ± 1 nm (Figure S13, Supporting Information). Because of a limited time resolution of the measurements in few millisecond domain, it is hard to evaluate the exact value of charge transfer rate at the surface. However, the increase of TA profile in the deeper trap state is attributed to the trap-limited recombination in the sub-microsecond time domain.^[44] This TA analysis indicates that the photogenerated holes at the surface-trap states in the Au-BVO photoanode have longer lifetimes, leading to enhanced hole transfer kinetics at the BVO/electrolyte interface.^[44,55]

3. Conclusion

In conclusion, incorporating a highly ordered hexagonal patterned Au nanosphere array into a metal-oxide-based electrode, BVO in the present study, results in simultaneous enhancements in the photon absorption, charge transport, and charge transfer. BVO was deposited at the central hot spot between the Au nanospheres in the patterned array, where the strong electric field was localized. To understand the optical and charge carrier dynamics associated with the PEC performance of the photoanode, we thoroughly investigated the effect of incorporating the Au nanosphere patterned arrays. The enhanced absorptance of the Au-BVO photoanode was found to originate predominantly from the LSPR effect of the Au nanosphere array. The Au nanosphere array also enhances the electron transport properties and charge transport efficiency through PIRET. The effect of PIRET was confirmed by time-correlated single photon counting and transient absorption studies, showing that the presence of the Au nanosphere array increases the characteristic lifetimes of both electrons and holes. As a result, incorporating the Au nanosphere array increases the photocurrent density of Mo:BiVO₄ at 1.23 V versus RHE by \approx 2.2-fold (2.83 mA cm⁻²), comparable with most of the other hybrid Au/metal oxide photoanodes in the literature. Our report demonstrates that the nanopositioning metal oxides, with respect to plasmonic metal

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nanostructure arrays, greatly enhance to the overall PEC water oxidation performance by improving both light harvesting and charge carrier dynamics. We believe that the plasmonic Au nanostructures can be further optimized to enhance light absorption and facilitate the direct electron transfer mechanism to contribute to the PEC performance.

4. Experimental Section

Fabrication of Au Nanosphere Patterned Array: A nanopatterned silicon wafer master substrate composed of a highly ordered hexagonal array of pillars with a diameter of 260 nm, a height of 260 nm, and a pitch of 520 nm was fabricated using a reactive ion etching lithography technique combined with KrF scanning. The prepared pattern master was replicated on an ultraviolet-curable PUA, (NOA 63, Norland Products, Inc.), which was uniformly dispersed on a PET substrate by UV nanoimprinting lithography.[56,57] The pillar-patterned array was imprinted on the PMMA-coated FTO glass by stamping the prepared PUA mold under a pressure of 2 kgf. An O₂ plasma treatment for 1 min (Gala Prep 5 with 17 VAC, 16 A, 60 Hz) was conducted to etch the PMMA pattern until the FTO underneath the hole was exposed. After removing the residual PMMA layer using an O₂ plasma treatment, the pores were filled with Au by electrochemical deposition from a 15×10^{-3} M HAuCl₄ (HAuCl₄·3H₂O, Aldrich) aqueous precursor in a three-electrode system under a constant voltage of -1.4 V (versus Ag/AgCl) with a Pt wire as the counter electrode. Consequently, a patterned array of Au nanospheres was obtained after calcination at 500 °C for 30 min.

Fabrication of Photoanodes Incorporated with the Au Nanosphere Patterned Array: The precursor solution used to deposit the BVO layer was prepared from stoichiometric bismuth nitrate hexahydrate (0.519 g, Aldrich), vanadyl acetylacetonate (0.273 g, Aldrich), and ammonium heptamolybdate (0.0076 g, Aldrich) in 10 mL of a mixed solvent of 1:0.12 acetylacetone (Aldrich) and glacial acetic acid (Aldrich). After 30 min of sonication, the precursor was spin-coated onto the Au nanosphere patterned array at 2000 rpm for 30 s, followed by step-wise annealing from 100 to 400 °C with an interval of 100 °C every 10 min, then annealing at 500 °C for 2 h. The thickness of BVO was determined by the number of repetitions of the spin-coating and annealing process. BVO films with thicknesses of 100, 220, and 350 nm were obtained via 3, 9, and 15 repetitions of the process, respectively.

PEC Measurements: The electrochemical measurements of LSV, CV, IPCE for EQE, and EIS were carried out using 0.5 M phosphate buffer electrolyte (pH 7.4), an Ag/AgCl reference electrode, and a Pt wire counter electrode under front-side (electrolyte-side) illumination. To characterize the charge transfer and the charge transport efficiency, 1 ${\mbox{\scriptsize M}}$ NaHCO3 was exploited as the hole scavenger. $^{[30-33]}$ The charge transport efficiency was obtained using $\eta_{transport} = J_{scavenger}/J_{abs}$, and the charge transfer efficiency was obtained using $\eta_{\text{transfer}} = J_{\text{water}}/J_{\text{scavenger}}$ and J_{abs} is the absorbed maximum photocurrent density from the light absorptance of each sample. A Model 660 (CHI Instruments Inc.) and a Gamry Interface 1000 Potentiostat (Gamry Instruments Inc.) were used as electrochemical instruments to measure the LSV and CV, respectively. A Polarnoix K3100 IPCE Measurement System (McScience Inc.) with a 300 W Xe lamp as a monochromator was used for the IPCE measurements.^[7] An electrochemical interface and impedance analyzer (CompactStat.h, Ivium Tech.) was used for the EIS measurements. The frequency was from 1 MHz to 0.1 Hz with 1.23 V versus RHE applied bias under simulated 1 sun illumination (100 mW cm⁻²). The observed spectra were fitted by using Z-view software. For the fitting of Nyquist plot, the constant phase element (CPE), a nonintuitive circuit element, was used instead of a pure capacitor in the simulations. The active area of 0.8 cm² was defined by insulating all surfaces besides the test surface with an opaque epoxy resin (Hysol) or was precisely defined using an aperture with an area of 0.28 cm². The EQE and IQE were calculated using the following equations

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$$EQE(\%) = \frac{n_{photocarriers}}{n_{incident photons}} \times 100(\%) = \frac{1240 J_{ph}(\lambda)}{P(\lambda)\lambda} \times 100(\%)$$
(1)

$$QE(\%) = \frac{n_{photocarriers}}{n_{adsorbed photons}} \times 100(\%) = \frac{1240 J_{ph}(\lambda)}{P(\lambda) \lambda \alpha(\lambda)} \times 100(\%)$$
(2)

where $n_{\rm photocarriers}$, $n_{\rm incident\ photons}$, and $n_{\rm adsorbed\ photons}$ are the numbers of photocarriers, incident photons, and adsorbed photons, respectively. $J_{\rm ph}(\lambda)$, $P(\lambda)$, $\alpha(\lambda)$, and λ are the photocurrent density, power density of incident light, absorptance, and wavelength of light, respectively.

Characterization: Scanning electron microscope (SEM) images were obtained by an FEI Helios focused ion beam (FIB) SEM and FEI XL30 Sirion SEM. For the FIB milling, Pt was deposited using a twostep deposition process: electron-beam-induced deposition (EBID) and ion-beam-induced deposition (IBID). Due to the high energy from the IBID, the surface of the first Pt layer deposited by EBID was slightly damaged during the second Pt layer deposition, as shown by the dark layer between two Pt layers in the cross-sectional SEM images. TA spectroscopy was carried out by femtosecond ultrafast pulses at 1030 nm generated by a fiber-based amplifier system (IMPULSE Femtosecond Laser by Clark MXR). The laser pulses with 100 fs pulse duration at a repetition rate of 1 MHz were split into two beams. The first beam was transformed to a 515 nm (±10 nm) green visible laser by a second harmonic generating (frequency-doubling) crystal for the pump pulse, and the second beam was focused into an undoped yttrium aluminum garnet (YAG) crystal to generate supercontinuum white light and filtered by a band pass filter, passing the wavelength of 630 nm for the probe pulses. The pump and probe beams were focused on the sample with diameters of $\approx 10 \ \mu m$. The probe light was detected by a photodiode with the same bandpass filter to filter out the pump pulse. The pump-probe time delay was controlled by a motorized linear delay stage, and the pump-probe signal was recorded using a lock-in amplifier with a mechanical chopper at a frequency of 700 Hz. For the longer time domain of TA characterization up to near millisecond scale, the sample was examined by a continuous wave (CW) laser. This study first generated 1 kHz square wave modulated 400 nm diode laser by function generator for the sample excitation (pump). The square wave and the diode laser response were sharp enough to turn on/ off the pump laser within 2 µs. This study also prepared CW He-Ne laser with wavelength 633 nm for the sample detection (probe). The two beams were focused at the sample with an objective lens into the same circular beam spot with diameter $\approx 2 \,\mu m$ and intensity about both 250 μ W. The reflected probe beam from the sample was gathered by same objective lens, passing through the edge filter which blocks the pump beam, and detected by time-sensitive photodiode (Thorlabs, DET 10A) to measure the time-dependent reflection change of the probe at the moment of turning on and off the pump. Signal was amplified by low-noise amplifier (Stanford Research, SR560) and sent into an electrical oscilloscope which can accumulate the signal over thousands of times for noise reduction. The low-temperature (20 K) TCSPC measurement was performed to investigate the photoluminescence (PL) decay using an ultrafast detection system comprised of a TCSPC module (PicoHarp, PicoQuant) with an MCP-PMT (R3809U-59, Hamamatsu). The PL emission was spectrally resolved using some collection optics and a monochromator (SP-2150i, Acton). The total instrument response function (IRF) was less than 140 ps, and the temporal time resolution was 16 ps. The deconvolution of the actual decay and IRF was carried out using software (FlouFit, PicoQuant) to deduce the time constant associated with each exponential decay.^[42,43,58] UV-vis spectroscopy was carried out on a Varian Cary 5000 UV-vis-NIR spectrophotometer to investigate the diffuse reflectance and the diffuse transmittance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



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Conflict of Interest

The authors declare no conflict of interest.

Keywords

gold nanospheres, pattern arrays, photoelectrochemical water splitting, plasmonic coupling, plasmon-induced energy transfer

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