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Electrochemical Imaging of Photoanodic Water Oxidation Enhancements on TiO₂ Thin Films Modified by Sub-Surface Al Nano-Dimers

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ABSTRACT: Detecting metal plasmonic enhancements on the activity of semiconducting photoanodes for water oxidation is often obscured by the inherent electroactivity and instability of the metal in electrolyte. Here, we show that thin TiO_2 photoanodes modified by sub-surface Al nano-dimers (AlNDs) display enhancements that are consistent with plasmon modes. We directly observed enhancements by mapping the oxygen evolution rates on TiO_2 /AlND patterns

using scanning electrochemical microscopy (SECM) while exciting the surface plasmons of the nanodimers. This study highlights the importance of sample configuration for the *in-situ* characterization of metal/photoanode interactions and suggests a route for Al-based plasmonics applied to photoelectrochemistry.

KEYWORDS: scanning electrochemical microscopy, oxygen evolution, surface plasmons, aluminum nanoparticles, water oxidation, thin film

Wide-bandgap semiconductors, such as TiO₂ and other titanates, are excellent materials for photo-assisted electrochemical water oxidation with ultra-violet (UV) light.^{1,2} However, UV light accounts for less than 7% of the solar spectrum. Strategies such as metal co-catalysis,³⁻⁵ dye sensitization,^{6,7} and ion doping,^{8,9} have been reported for improving the reactivity and photoactive spectrum of these materials. In the last decade, progress in the understanding of surface plasmons supported by metal nanostructures, has led to considerable interest in harnessing their interactions with semiconductors.¹⁰⁻¹⁴ Plasmonic field enhancement and plasmon induced electron transfer are two predominant mechanisms for the amplification of photoactivity introduced by the metal.¹⁵⁻¹⁹ In addition, defects,^{20,21} rectifying junctions,^{22,23} and photothermal effects²⁴ also contribute to these enhancements. Nanostructures of Au and Ag have been reported to improve the photoelectrochemical activities of titanates and hematite.²⁵⁻³¹ However, the performance of such configurations were still bound by the limited plasmonic tunability of noble metal nanostructures and severe plasmonic damping.³² Additionally, it remains unclear whether these previous works fully decoupled plasmonic enhancements from

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effects due to the inherent electrochemical activity of the metal.^{33,34} These examples demonstrate the need for experiments that incorporate metal nanostructures with wide plasmonic tunability together with *in-situ* electrochemical methodologies that elucidate the role of the metal on water splitting reactions.

Recently, Al plasmonic nanostructures have attracted attention not only because this metal is abundant and inexpensive, but also because Al exhibits plasmonic behavior across a wide spectrum from the ultraviolet (UV) to the near infrared (NIR).³⁵⁻³⁸ Al shows strong interband transitions within a narrow band in the NIR at 1.5 eV,³⁹ imparting Al nanoparticles a wide plasmonic tunability. However, the chemical instability of Al towards dissolution at extreme pH conditions and highly oxidizing potentials is a source of concern for its coupling to a photoanode. Nevertheless, a theoretical study on a core-multishell nanowire photoelectrode made of Si/Al/Fe₂O₃ for water splitting predicts a solar to hydrogen efficiency of up to 14.5%,⁴⁰ clearly making the study of Al-modified photoelectrodes of interest. To the best of our knowledge, experimental studies regarding Al nanostructures for plasmon-enhanced water oxidation have not been reported.

In this article, we develop a hybrid system utilizing dimers of Al nanoparticles, here referred to as "Al nanodimers" (AlNDs), underneath a TiO_2 thin film as an experimental demonstration of Al-based plasmon-enhanced water oxidation. A TiO_2 film was deposited on top of patterned AlNDs to act as the photocatalyst and protect the AlNDs from dissolution. AlNDs were used to support surface plasmons so that local photocurrent can be enhanced through either optical field enhancement or plasmon-induced electron injection. The structure of dimer was chosen due to their optical polarization sensitivity, which allowed us to probe the plasmonic nature of interactions with TiO₂. In addition to typical bulk photoelectrochemical measurements,

we mapped the local oxygen evolution rates using the substrate generation/tip collection (SG/TC) mode of scanning electrochemical microscopy (SECM).⁴¹⁻⁴³ Spatially-resolved SECM images showed a modulation of oxygen evolution rates as a function of the excitation of distinct plasmonic modes over AlND patterns.

RESULTS AND DISCUSSION

Topographic Characterization

AINDs were fabricated on an indium tin oxide (ITO) – coated glass substrate using a topdown method based on electron-beam lithography (EBL) and lift-off procedure. The dimers were written in an array of 40 μ m × 40 μ m with a spacing of 500 nm. The gap size between the units in each dimer was 16 nm \pm 2 nm, and each unit had a size of 70 nm \pm 3 nm in diameter and 50 nm in height. The surface coverage of Al, *i.e.*, area taken up by AlNDs divided by the area of one μ m × 40 μ m pattern, was about 3.1%. This represented only 0.67% for the entire 0.28 cm² substrate exposed to solution. Compared to self-assembling of nanoparticles, the EBL method allow us to write nanodimers in a regular array with clear boarders of patterned/unpatterned areas and uniform dimer orientations, which are the prerequisites for us to recognize the pattern from SECM images and to obtain a polarization-sensitive oxygen concentration. After nanoparticle fabrication, the sample was coated with 50 nm-TiO₂ using atomic layer deposition (ALD) at 200°C. A sample consisting of Au nanodimers (AuNDs) in the same configuration was prepared as a control experiment. The nanostructures were characterized with scanning electron microscopy (SEM). Fig. 1a shows the SEM image of Al nano-dimers deposited on ITO. Fig. 1b and 1c are SEM images of a small region within the array of AlNDs and AuNDs before TiO_2

deposition, respectively, while Fig. 1d and 1e are the SEM images of the AlNDs and AuNDs after TiO_2 deposition, respectively. These images show that the morphology and geometry of both types of substrates are similar.



Figure 1. (a) SEM characterization on the arrays of AlNDs. Zoomed-in SEM images on the (b) AlNDs and (c) AuNDs, before TiO_2 deposition. SEM images on the (d) $TiO_2/AlNDs$ and (e) $TiO_2/AuNDs$ after TiO_2 deposition.

For photoelectrochemical experiments, the incident light was introduced from a Hg(Xe) lamp (Model 67005 with a 300 W 6292 Hg(Xe) Ozone Free bulb) with UV and visible light components to the bottom of the substrate by an optical fiber that was coupled to a $15 \times /0.32$ NA UV-enhanced objective. The beam spot at the surface of the sample was defocused to a size of 500 µm in diameter to ensure the illumination of the entire pattern. Because of the low coverage of nano-dimers and differences in substrate fabrication, full sample voltammograms in the dark

or under chopped illumination (Figs. S2 and S3) are less reliable than the selected-area photoaction and electrochemical imaging experiments discussed in the following sections. The irradiance at substrate surface plane was 765 mW•mm⁻² with no polarization dependence (Fig. S1). Photoelectrochemical experiments were performed in 0.1 M NaOH using a 0.5 mm-diameter Pt wire counter electrode and a Ag/AgCl reference electrode.

Photoaction Spectra

The photoaction spectra of 50 nm TiO_2 thin film on 1) AuNDs, 2) AlNDs, and 3) bare ITO-coated glass substrate were measured with the substrates biased to 0.5 V vs. Ag/AgCl, wellbelow the onset of electrocatalytic water oxidation on the bare metals, and are shown in Fig. 2a and 2b. Without any metal nanoparticles, TiO_2 -coated ITO substrate (Fig. 2 in black) is photoactive within the band of 300-470 nm and the photocurrent peaks at 350 nm with a small tail from 400 to 470 nm. The presence of nanoparticles enhances the photoactivity of TiO₂ within the band of 380-500 nm, where AINDs (Fig. 2a in red) shows a larger modification than AuNDs (Fig. 2b in blue). Fig. 2c overlays the scattering spectrum with the photoaction spectrum of the TiO₂/AINDs pattern. The scattering spectrum of TiO₂/AINDs was measured with the help of a photomultiplier and a monochromator that was coupled to a confocal microscope. Peaks at 425 nm and 400 nm can be assigned to the longitudinal and transverse modes of surface plasmons of the nanodimers, respectively.^{44,45} The photocurrent of AlNDs-modified TiO₂ thin film and the plasmon resonances of AlND have a spectral overlap within the band of 370-435 nm. In other words, the surface plasmons of AIND contribute more efficiently to the photocurrent within this waveband than other wavelengths. Enhancements on the photocurrent within the band of 440-500 nm are likely due to off-resonant plasmonic enhancements. Fig. 2d overlays the photoaction spectrum with the scattering of $TiO_2/AuNDs$. Clearly, almost no overlap exists between the

photoactivity of TiO_2 and the main plasmon resonance of the AuNDs in the visible. The scattering peak at about 710 nm is assigned to the transverse plasmon mode. The longitudinal mode appears in the infrared and is beyond working area of the spectrometer. A simulated spectrum is provided in Fig. S4 in the Supporting Information.



Figure 2. (a) Scattering spectrum collected from single array of $TiO_2/AINDs$ (in green) overlays with the photoaction spectrum of the $TiO_2/AINDs$ sample (in red) and TiO_2 -coated ITO substrate (in black). (b) Scattering spectrum collected from single array of $TiO_2/AIND$ (in violet) overlays with the photoaction spectrum (in blue) collected from the $TiO_2/AuNDs$ sample. TiO_2 - coated ITO substrate (in black) is provided here again as a reference.

Local Oxygen Mapping Using SECM

In order to directly observe water oxidation enhancements on the TiO₂ areas modified by sub-surface metals, we measured local oxygen evolution rates over the patterns using scanning electrochemical microscopy, a chemically-sensitive *in situ* technique with spatial resolution. We used a Hg-capped⁴⁶⁻⁴⁹ submicron Pt-in-glass electrode (Pt wire 600 nm in diameter) due to its excellent stability for O_2 collection (Fig. S5 in the Supporting Information). The tip (RG = 10) was positioned 1.32 µm above the sample surface with a negative feedback approach curve using residual O₂ from air as redox probe, and fitted to theory (Fig. S6).⁵⁰ Tilt in the X-Y plane was removed prior to imaging to c.a. 0.3 µm/mm. The SECM setup counted with a video microscope for positioning the probe near the dimer-modified areas (Fig. S7). The substrate was biased at 0.5 V (vs. Ag/AgCl) for oxygen generation and the Hg working electrode was biased at a potential of -0.74 V (vs. Ag/AgCl) for oxygen collection during SECM imaging. In order to unambiguously identify the array, the substrate was rotated 45° in the XY plane of the SECM image. Polarization of incident light was either along the long axis (Fig. 3a, longitudinal) or short axis (Fig. 3b, transverse) of the AINDs. SECM images and lateral scans were performed with an increment distance of 1 um and an increment time of 0.02 sec. Tip current due to oxygen collection measured in darkness above the AIND array (Fig. 3c) shows that without illumination, only environmental oxygen is detected (*i.e.* residual O₂ from air). Upon illumination, an evident contrast appears between the pattern of AlNDs under TiO₂ thin film and the unmodified TiO₂ bulk. We attribute this contrast mainly to plasmonic effects including 1) the local optical field enhancement on Al pattern and, 2) plasmon-induced hot electrons. Other effects such as defects at the metal/semiconductor interface, photothermal effects, etc., may cause a general enhancement on TiO₂ photoactivities, but are less likely to show optical polarization dependence.

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Overall, a 27.8% enhancement on the photocurrent caused by the transverse mode surface plasmons supported by AlNDs can be thus deduced. It is worth noting that this enhancement resulted from an extremely low AlND surface coverage of 3.1%. Thus, an enhancement factor of about 9 (27.8%/3.1%) is estimated for individual AlND.

The optical near-field distribution is polarization-dependent due to the excitation of distinct plasmon modes. Although the transverse plasmon resonance is closer to the wavelength for maximum TiO₂ activity (Fig. 2) than the longitudinal plasmon resonance, we obtained a higher signal under longitudinal polarization. While this would lead us to predict little plasmonic enhancement of oxygen evolution rates by longitudinal modes, electric field confinement in the gap of the dimer must be considered when the plasmons are driven by longitudinal polarization.^{51,52} For these dimers, the gap confinement tends to have a larger enhancement on the photocurrent than the transverse plasmon resonance, as we will discuss in the numerical simulation section.



Figure 3. SECM image on TiO₂/AlND pattern (a) with longitudinal polarization, (b) with transverse polarization, and (c) in darkness. Control experiment: SECM tip current measured from TiO₂/AuND pattern (d) longitudinal polarization, (e) with transverse polarization, and (f) in darkness. Scale bars represent 20 μ m. Black double arrows show the incident polarizations. Dashed squares represent the border of patterned region.

To highlight the effect caused by the AlNDs, a control experiment on a similar pattern of AuNDs was carried out. Fig. 3d and 3e again demonstrate the tip current due to oxygen collection measured on top of the AuND pattern under longitudinal and transverse polarizations, respectively. Fig. 3f is the tip current mapping of AuND pattern in darkness. Unlike the AIND patterns above, the tip did not detect clear enhancements in the oxygen evolution rates above the TiO_2 -coated Au pattern. The tip only measured the background activity of the TiO_2 substrate and residual O₂ in solution. We believe the plasmonic near-field enhancement is prevented because the strong interband transition of Au under wavelength of $\lambda < 500$ nm that leads to the damping of surface plasmons. It should be noted that although the light source has considerable output intensity at wavelength of $\lambda > 500$ nm, the TiO₂ layer in our study does not show obvious photoactivity in this band (Fig. 2). As a consequence, the patterns of AuNDs cannot generate strong enough field enhancement to distinguish them from the TiO₂ background on the oxygen concentration map. Critically, this experiment was carried out with Au nanoparticles excluded from direct contact with the electrolyte, so that Au has no co-catalytic contributions to the photocurrent enhancement.²⁵⁻³¹ In the Supporting Information (Figs. S6 and S7) we provide an additional reference study on TiO₂ nanoparticles that were drop-casted on AuND patterns. These spatially-resolved experiments confirm the electrocatalytic activity of Au in darkness and the photo-activity of TiO₂ nanoparticle/AuND system. An equivalent experiment with TiO₂

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nanoparticles on AlNDs was impossible because aluminum dissolved immediately when in contact with the electrolyte. The $TiO_2/AlND$ substrate was intact after experimentation in electrolyte (Fig. S10). These observations highlight the advantage of using a direct technique to verify the *in-situ* generation of O_2 and the importance of studying plasmonic effects using the sub-surface approach and under strictly-controlled conditions for the metal and electrolyte.

To further explore the polarization dependence of photocurrent, the background subtracted cross-section profiles of Fig. 3a and 3b are plotted in Fig. 4. No polarization sensitivity was observed from the bare TiO_2 layer on the ITO substrate (Fig. S1). By simply rotating the incident polarization from short axis to long axis of the nanodimers, we obtained a 43% extra enhancement on the tip current. We attribute this difference to the plasmonic confinement created at the nano-dimer gap.



Figure 4. Baseline-corrected tip current profiles under illumination with longitudinal polarization (in red) and transverse polarization (in blue). The profile was obtained from the diagonal of the pattern shown by the dashed line in the inset. Data previous to subtraction is available in Fig. S11 in the Supporting Information.

Finite-Difference Time-Domain Simulations

To confirm the plausibility of the observed enhancements we simulated the optical electromagnetic field distribution near AINDs using the 3-dimensional finite-difference timedomain method (3D-FDTD) under wavelengths from 300 nm to 500 nm, with a step of 10 nm. Fig. 5 shows the simulated optical near-field distribution at wavelengths of $\lambda_0 = 350$ nm (Fig. 5a, b), 380 nm (Fig. 5c, d), 430 nm (Fig. 5e, f), and 480 nm (Fig. 5g, h). Either a longitudinal (left column) or a transverse (right column) polarization of incident light was applied in the simulation. The AlND was placed on top of ITO substrate and covered by TiO₂. The 3D-FDTD simulation was performed using a 2 nm \times 2 nm \times 2 nm mesh. The volumes of ITO substrates in Fig. 5 are hidden in order to highlight the optical near-field distribution in the region of interest, *i.e.*, in the TiO₂ layer. The original simulated results are provided in Fig. S12. At 350 nm and 380 nm, the transverse mode tends to show a higher enhancement than the longitudinal mode, especially at the bottom of the gap. At 430 nm and 480 nm, the enhancement under transverse polarization decreases, while enhancement under longitudinal polarization increases with increasing wavelength. Compared to the transverse mode, the field confinement under longitudinal polarization enhances the entire gap of the dimer.



Figure 5. 3D-FDTD simulation of the local optical near-field distribution of AlND on ITO substrate in an environment of TiO₂. The simulation was performed at wavelengths of (a, b) $\lambda_0 = 350$ nm, (c, d) $\lambda_0 = 380$ nm, (e, f) $\lambda_0 = 430$ nm, (g, h) $\lambda_0 = 480$ nm with distinct incident polarizations exciting the longitudinal (left column) and transverse (right column) plasmon modes, respectively. A mesh of 2 nm × 2 nm × 2 nm was applied for simulation. Unit vectors E_0 and k show the polarization and the propagating direction of the incident light, respectively. Dashed lines represent the Al/TiO₂ interfaces. The volumes of ITO substrates are covered by white semitransparent masks. Scale bars represent 50 nm.



Figure 6. (a) Plot of maximum field intensity enhancement factor as a function of wavelength under longitudinal (red dot) and transverse (blue square) polarizations. (b) Optical near-field-enhanced normalized photocurrent as a function of wavelength. The AIND is 70 nm in diameter and 50 nm in height with a gap size of 16 nm.

A semi-quantitative view of the impact of plasmonic enhancements on the photocurrent follows. The maximum electric field intensity enhancement factor $EF(\lambda)$ is plotted in Fig. 6a as a function of wavelength. Field distributions in the ITO substrates were not considered for the maximum electric field intensity enhancement factor. Therefore, we calculated the optical nearfield-enhanced normalized photocurrent $I_{nf}(\lambda)$ by multiplying the optical near-field intensity

enhancement factor $EF(\lambda)$ by the normalized photocurrent of bare TiO₂ layer (black curve in Fig. 2a). The calculated $I_{nf}(\lambda)$ are plotted in Fig. 6b under either longitudinal (red dot) or transverse (blue square) polarizations. A detailed process of normalization is described in Supporting Information. We integrated the near-field-enhanced normalized photocurrent within the photoactive region ($\lambda = 300$ nm to 500 nm) to obtain an overall $I_{nf}(\lambda)$ of 7.37 for longitudinal mode and 5.99 for transverse mode. A polarization sensitivity of 23% was deduced theoretically against the 43% obtained experimentally. An unavoidable passivating layer of Al_2O_3 with dimensions of 2-3 nm in thickness is likely to be present on the surface of the AlNDs, thus contributing to reducing the efficiency of electron injection into TiO₂ from plasmon-induced hot electrons. A control experiment in which an additional pinhole-free 10 nm layer of Al_2O_3 was grown on AlNDs below a layer of TiO₂ showed a weakened photoactivity within the band of 380 -500 nm. However, it has been reported that the growth of Al₂O₃ on plasmonic Al structures red-shift their resonance as much as 15 nm for a 3 nm layer,³⁶ possibly shifting the AlND/Al₂O₃ resonance further outside the TiO₂ photoactive spectrum. These results suggest that other possible contributions, such as plasmon-induced hot electrons, could be concurrent to near-field enhancements. Nonetheless, the highly localized nature of the electrochemical enhancements on TiO₂, the observed polarization sensitivity, and the lack of direct interaction of the AlNDs with the electrolyte, give strong evidence for near-field enhancements mediated by the sub-surface metal.

CONCLUSION

In conclusion, we reported near-field enhancements on the photoelectrochemical activity of thin TiO₂ films modified by electrolyte-excluded sub-surface Al nanodimers. By mapping the oxygen evolution rates on the TiO₂/AIND substrate using SECM while exciting the transverse plasmon mode of the nanodimers, we directly observed a 27.8% increase in the local oxygen evolution rate despite a low AIND surface coverage of 3.1%. Although excited off-resonance, the optical near-field under longitudinal polarization yielded an additional contribution. It is noteworthy, that the sub-surface design of our experiment precluded the possibility that Al dissolved or that it engaged directly in electrochemical activity. Unlike Au, which did not show activity in the sub-surface but showed enhanced currents in the dark when exposed to electrolyte, AINDs yielded a distinctive response that was consistent with near-field enhancements. Looking ahead, because the Al interband transition happens only in a narrow band in the NIR, the localized Al surface plasmon resonances can be further tuned by varying nanoparticle sizes or shapes to match the photoactivity of a wide variety of semiconductor photoelectrodes.

METHODS

Chemicals

Sodium hydroxide (97+%), mercury(II) nitrite monohydrate, and potassium nitrate (\geq 99%) were obtained from Sigma-Aldrich. Nitric acid was obtained from Avantor. Millipore-filtered water was used in all experiments.

Electron-beam lithography and metal deposition

The ITO-coated glass substrate was sonicated in acetone, ethanol and isopropanol for 15 min each. Polymethyl methacrylate (PMMA)was spin-coated on the cleaned substrate with a speed of

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3000 rpm and an acceleration of 4000 rpm/s for 30 seconds. The PMMA-coated sample was then placed on hotplate to heat at 175 °C for 30 min. Nano-patterns were designed and exposed with the Raith e-Line micro and nanofabrication system at Frederick Seitz Materials Research Laboratory with a high tension of 10 kV, working distance of 10 mm, and beam current of 0.21 nA. After electron-beam exposure, the sample was developed with a mixed solvent of methyl isobutyl ketone (MIBK) and isopropanol with a volume ratio of 1:3 for 60 sec. It is then rinsed with isopropanol for 20 sec and dried with nitrogen. The sample was then deposited with either aluminum (99.999%) by thermal evaporation at a coating rate of 0.2 nm/s under a high vacuum of 4×10^{-6} Torr, or gold (99.99%) by sputtering at a rate of 0.17 nm/s under a high vacuum of 3×10^{-6} Torr. The metal-coated sample was immersed overnight in acetone for lift-off. It was then rinsed by isopropanol and dried with nitrogen.

Scattering spectrum of Al nanoparticles

The scattering spectrum on the Al nanodimer pattern was collected with a photomultiplier that was coupled to a confocal microscope (Zeiss LSM 880 Airyscan). The same Hg(Xe) lamp for SECM images was used as light source. This system allows the collection of optical images in any selected waveband (5 nm minimum bandwidth) between 365 nm and 700 nm. We collected a series of optical images of the sample with different waveband of detection. The intensity can be read from each pixel of these images. By subtracting the intensity on the background from that on the pattern of Al nanodimers each optical image, we can plot the scattering spectrum of the Al nanodimers in Fig. 2.

Hg working electrode preparation

The fabrication of Wollaston electrode was fabricated following the procedures described in reference.⁵³ A glass capillary was pulled with a fiber puller (P-2000 Shutter Instrument Co.) to obtain a sharp tip with aperture (sub micrometer scale) at one end. A Wollaston wire was placed into the capillary to the end of the tip. Then the sharp end of the capillary was put into a solution of HNO₃:H₂O (1:1 volume ratio). Through capillary forces the solution began to fill capillary and was allowed to immerse half of the Wollaston wire then removed from the solution. Five minutes were allowed to dissolve the Ag coating, leaving only the 600 nm diameter Pt wire. After removing the solution, the Wollaston wire was sealed inside the capillary with a heated metal coil. The Wollaston wire was connected to a copper-tin lead by Ag epoxy. The tip was then kept in an oven at 120°C for 4 hrs. Before Hg deposition, the Wollaston electrode was polished with 100 nm diamond particles over a polishing pad. The Hg cap was deposited using electrochemical method in references ⁴⁶⁻⁴⁹. From an aqueous solution of 5 mM Hg(NO₃)₂, 0.1 M KNO₃, and 0.5 vol % HNO₃, Hg was deposited on the Wollaston tip at -0.1 V (*vs.* Ag/AgCl) for 20 sec. A Tungsten wire was used as counter electrode for Hg deposition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information provides 1) amperometric i-t curve with interrupted illumination on TiO₂-coated bare ITO substrate showing optical polarization independence; 2) cyclic voltammogram in darkness at the electrodes of TiO₂/AlND, TiO₂/AuND, and bare ITO substrate; 3) photocurrent bulk measurements on the AlND/TiO₂, AlND/TiO₂, and TiO₂/ITO electrodes; 4) simulated spectrum of TiO₂/AuND; 5) Hg-capped SECM probe characterization; 6) Sample

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alignment and probe positioning; 7) probe approach curve of the Hg tip; 8) a control experiment on TiO₂ nanoparticle that were drop-casted on a small pattern of AuNDs; 9) SEM image on the TiO₂/AlNDs after all electrochemical measurements completed; 10) original tip current crosssection profiles of TiO₂/AlND pattern; 11) 3D-FDTD simulation method and the original images of the simulated electromagnetic field distribution; 12) normalization of photocurrent; 13) X-ray fluorescence for elemental analysis; and 14) control experiments with Al₂O₃ insulating layer. The supporting Information is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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