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Article

TiO₂-HfN Radial Nano-Heterojunction: A Hot Carrier Photoanode for Sunlight-Driven Water-Splitting

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Abstract: The lack of active, stable, earth-abundant, and visible-light absorbing materials to replace plasmonic noble metals is a critical obstacle for researchers in developing highly efficient and cost-effective photocatalytic systems. Herein, a core-shell nanotube catalyst was fabricated consisting of atomic layer deposited HfN shell and anodic TiO₂ support layer with full-visible regime photoactivity for photoelectrochemical water splitting. The HfN active layer has two unique characteristics: (1) A large bandgap between optical and acoustic phonon modes and (2) No electronic bandgap, which allows a large population of long life-time hot carriers, which are used to enhance the photoelectrochemical performance. The photocurrent density ($\approx 2.5 \text{ mA}\cdot\text{cm}^{-2}$ at 1 V vs. Ag/AgCl) obtained in this study under AM 1.5G 1 Sun illumination is unprecedented, as it is superior to most existing plasmonic noble metal-decorated catalysts and surprisingly indicates a photocurrent response that extends to 730 nm. The result demonstrates the far-reaching application potential of replacing active HER/HOR noble metals such as Au, Ag, Pt, Pd, etc. with low-cost plasmonic ceramics.

Keywords: plasmonic catalysis; hot carrier absorber; ultraviolet photoelectron spectroscopy; density functional theory; FDTD electromagnetic simulations; transition metal nitrides



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1. Introduction

The group IV transition metal nitrides are beginning to attract a great deal of attention due to their unique characteristics such as exhibiting both metallic and semiconducting properties, possessing ceramic hardness, high thermal tolerance, and chemical resistance, showing the possibility for substitution of plasmonic noble metal, etc. [1,2]. Notwithstanding all the advantages, there have been rather few practical applications demonstrated. Most studies in the field have focused on material synthesis and characterization [3,4]. Among all the transition metal nitrides, titanium nitride is by far the most studied and utilized material [5–7], while hafnium nitride is basically unexplored and rarely utilized in optoelectronic devices. There are many reports investigating approaches to synthesize high-quality HfN. We are interested in employing HfN as a hot carrier absorber because its wide phonon gap can slow down the carrier thermalization process. Saha et al. calculated its electronic structure indicating its unique phonon dispersion of acoustic and optical branches [8]. Based on this feature, Chung et al. proposed using HfN in hot carrier solar cells and obtained a decay time of 1.7 ns in a transient absorption spectroscopic measurement [9]. The one and only catalytic application report was from Chiara et al., in which HfN

nanoparticles were used for electrocatalytic oxygen evolution, and the highest performance was $10 \text{ mA}\cdot\text{cm}^{-2}$ at an overpotential of 358 mV [10]. Another similar work was presented by Yang et al. reporting electrocatalytic hydrogen evolution using nitrogen-plasma-treated hafnium oxyhydroxide [11]. Based on the findings from pioneer studies, HfN is worth investigating as a photocatalyst for solar energy conversion due to the following reasons: (1) high thermal and chemical resistance, and photochemical stability under harsh conditions; (2) long hot carrier lifetime; (3) plasmon resonance in the Vis-NIR regime; and (4) cost-efficient alternative to noble metals. Despite the aforementioned properties that are particularly beneficial to photocatalytic energy conversion, no one has reported the successful utilization of HfN for any kind of photocatalytic reactions. With this aim in mind, a photoanode consisting of $\text{TiO}_2(\text{core})\text{-HfN}(\text{shell})$ nanotube arrays (HfN-TNT) was deployed in photoelectrochemical water splitting and achieved a champion photocurrent of $2.48 \text{ mA}\cdot\text{cm}^{-2}$ under 1 Sun illumination (AM 1.5G) at an applied bias of +0.6 V vs. Ag/AgCl reference electrode in 1 M KOH solution. A photocurrent response of $2.39 \text{ mA}\cdot\text{cm}^{-2}$ during light on-off cycling was measured under identical conditions. To the best of our knowledge, this performance is superior to most plasmonic noble metal-decorated TiO_2 -based catalysts. The TiO_2 nanotube array (core) was grown by electrochemical anodization of a Ti film sputtered at room temperature on a non-native fluorine-doped tin oxide (FTO)-coated glass substrate. The conformal HfN shell layer was formed by plasma-enhanced atomic layer deposition, which is a facile technique to form conductive transition metal nitride coatings of good structural and stoichiometric quality [12,13]. The catalyst is economically efficient and suitable for large-scale production due to the scalability and existing industrial usage of electrochemical anodization and atomic layer deposition.

Wide bandgap (WBG) metal oxides have been demonstrated to be photochemically stable, high-performance photocatalysts for artificial photosynthesis [14–17]. One-dimensional WBG architectures such as vertically aligned arrays of nanotubes and/or nanorods are established to be highly optimal from the point of view of solar energy harvesting and reduction of carrier recombination losses, since this architecture orthogonalizes the competing processes of light harvesting and charge separation [18,19]. However, the low visible light-harvesting ability of catalytically-active metal oxides such as TiO_2 , Nb_2O_5 , SrTiO_3 , KNbO_3 , etc. has motivated the search for visible light-harvesting heterojunction formers/co-catalysts that sensitize the photocatalyst to visible photons where the bulk of the solar energy resides. One strategy consists of forming core@shell heterojunctions wherein WBG nanotubes or nanorods (“core”) are coated with a thin absorbing layer of a lower bandgap semiconductor (“shell”) [20,21]. While core-shell heterojunctions have shown considerable promise in improving the performance of photoelectrochemical water splitting [22–24], photoanodes constituted exclusively of semiconductors suffer thermodynamic losses for supra-bandgap photons. On the other hand, photoanodes consisting of plasmonic metal-semiconductor heterojunctions can reduce thermalization losses by efficiently harvesting hot carriers while simultaneously sensitizing WBG semiconductors to visible photons [25,26]. Currently, plasmonic coinage metal (Au, Ag, Cu) nanoparticles [27–31] and 2D material nanosheets ($\text{g-C}_3\text{N}_4$, MoS_2 , etc.) [15,32–34] are the most commonly used, photochemically stable co-catalysts that are used to decorate nanostructured metal oxides and achieve the desired photosensitization. Coinage metals are very expensive and suffer from ultrafast hot carrier relaxation processes. Two-dimensional (2D) materials have low absorption coefficients and frequently require sacrificial agents for optimal charge transfer. We demonstrate here that plasmonic transition metal nitride ceramics, specifically HfN, form a third class of visible-light absorbing compounds which can be used to form heterojunctions with metal oxides that result in photocatalysts/photoelectrodes that combine intrinsic photochemical stability, low cost, and high performance without the need for a sacrificial agent or carrier scavenger.

2. Results and Discussion

2.1. Photoelectrochemical Performance

The photoelectrochemical J - V characteristics of HfN-TNT (shown in Figure 1a,b) were collected in the dark and under AM 1.5G 1 sun illumination without and with a UV filter in 1 M KOH solution. A baseline was measured without any illumination, in which we observed almost zero photocurrent density. The highest photocurrents (shown in Figure 1a) are $2.48 \text{ mA}\cdot\text{cm}^{-2}$ under 1 Sun illumination (AM 1.5G) and $1.8 \text{ mA}\cdot\text{cm}^{-2}$ after adding a UV filter ($>420 \text{ nm}$) at an applied bias of $+0.6 \text{ V}$ vs. Ag/AgCl. The data collected under light on–off mode is shown in Figure 1b, in which the photocurrents are $2.39 \text{ mA}\cdot\text{cm}^{-2}$ and $1.74 \text{ mA}\cdot\text{cm}^{-2}$ without and with a UV filter, respectively. To understand the spectral composition of the generated photocurrent, a set of near-monochromatic LEDs were used to illuminate the sample (Figure 1c,d) for testing that were conducted in 0.1 M KOH electrolyte and, unless otherwise stated, the photocurrents were at a bias of $+0.6 \text{ V}$ versus Ag/AgCl. We observed a photocurrent response that extended all the way to 730 nm wavelength illumination, which is quite unusual in the field of sunlight-driven water-splitting. The 730 nm photons have an energy of 1.7 eV , which is merely 0.47 eV above the minimum energy required for water electrolysis. It is important to understand how the performance of the HfN-TNT photoanodes stands in comparison to the plasmonic noble metal sensitized metal oxide photoanodes they seek to replace. Table 1 is a performance summary of the photoelectrochemical performance under visible light illumination of TiO_2 -based photoanodes that derived an enhancement of photoactivity in the visible regime after decoration by nanoparticles or coatings of plasmonic noble metals, namely Ag and Au. Table 1 shows that the harvesting of visible light using hot carriers by previously reported noble metal- TiO_2 nanostructured plasmonic heterojunctions is able to generate no more than $224 \mu\text{A}\cdot\text{cm}^{-2}$ in a photocurrent. Such a poor performance is not entirely surprising, since it is well-understood that the ultrafast timescale ($<10 \text{ ps}$) of electron–electron scattering and electron–phonon scattering render extremely hard to drive chemical reactions using hot carriers before their thermal equilibration. In contrast, our unoptimized HfN-TNT photoanode is able to generate $1.8 \text{ mA}\cdot\text{cm}^{-2}$ under identical conditions, as shown in Table 1, indicating a potentially superior hot carrier harvesting ability.

Table 1. A summary of photocurrent densities observed with plasmonic noble metal-decorated TiO_2 -based photoanodes for PEC water splitting under visible light illumination.

Sample	Photocurrent ($\mu\text{A}/\text{cm}^2$)	Light Intensity (mW/cm^2)	Light Spectrum	Applied Bias	Electrolyte	Reference
HfN-TNT	1800	100	visible light ($>420 \text{ nm}$)	0.6 V	1 M KOH	This work
Ag/N- TiO_2	26	120	visible light ($>420 \text{ nm}$)	0 V	0.5 M Na_2SO_4	[35]
AgNPs/ TiO_2 NWs	47	100	visible light ($>420 \text{ nm}$)	0.4 V	0.1 M Na_2SO_4	[36]
In situ AgNPs/TNTs	40	80	visible light ($>420 \text{ nm}$)	0.3 V	0.1 M Na_2SO_4	[37]
Ag/N- TiO_2	0.5	500	400–900 nm	0.3 V	1 M KOH	[38]
Au/RGO/H-TNTs	224	100	visible light ($>400 \text{ nm}$)	0.2 V	1 M KOH	[39]
LE-Au/TNTs	202	100	visible light ($>400 \text{ nm}$)	0.2 V	1 M KOH	[40]
AuNPs/ TiO_2	23	7000	532 nm, 633 nm	0 V	1 M KOH	[41]
Au embedded TiO_2	3		visible light ($>420 \text{ nm}$)	0.2 V	1 M KOH + 25% MeOH	[42]
AuNPs/ TiO_2 BNRs	125	100	visible light ($>420 \text{ nm}$)	0.5 V	1 M KOH	[43]
AuNPs/ TiO_2 NWs	11	73.3	visible light ($>430 \text{ nm}$)	0 V	1 M KOH	[44]
AuNPs/ TiO_2 PhC	150	100	visible light ($>420 \text{ nm}$)	0.2 V	1 M KOH	[45]

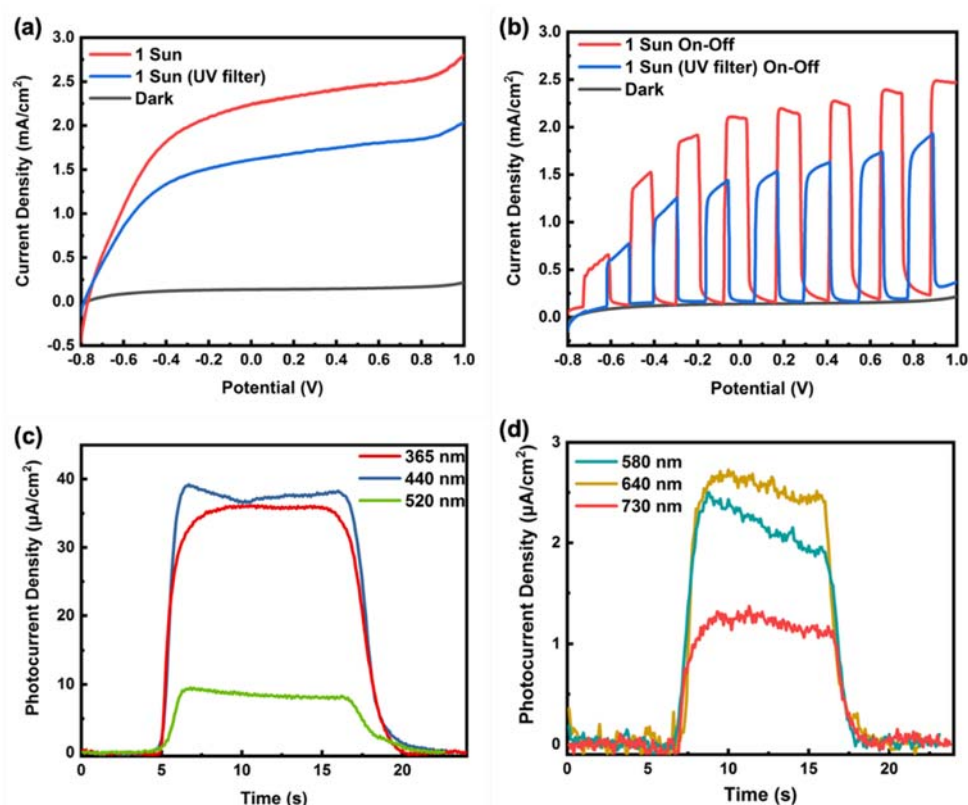


Figure 1. Photocurrent density plots: (a) Photocurrent measured by linear sweep voltammetry under AM 1.5G illumination; (b) Photocurrent response during light on–off cycles, measured by linear sweep voltammetry under AM 1.5G illumination with and without UV cut-off filter (>420 nm); (c,d) Amperometric *I*-*t* curves showing photocurrent response under the illumination of near-monochromatic LEDs above at 0.3 V vs. Ag/AgCl.

2.2. Physicochemical Characterization

The morphologies were examined before and after HfN coating using a Zeiss Sigma field emission scanning electron microscope (FESEM). The outer diameter of nanotubes is 80–100 nm, while the inner diameter is 30–50 nm (Figure 2a). After HfN atomic layer deposition (ALD), the mouths of nanotubes are almost closed, and the space between the nanotubes is filled. The high-resolution transmission microscopy (HRTEM) image (Figure 2c) shows the tubular structure with double layers. The TiO₂ core is slightly brighter than the HfN shell, which is darker. Figure 2d shows the lattice fringes at the interface of the core and shell with 0.358 nm and 0.256 nm interplanar d-spacing, corresponding to anatase TiO₂ (101) and HfN (111), respectively.

In the Hf 4f XPS spectrum (Figure 3a), the splitting of a spin orbit results in clear doublet peaks, which are Hf 4f_{5/2} and Hf 4f_{7/2}. Thus, the peaks at 16.9 eV and 18.6 eV can be assigned to Hf 4f_{7/2}-N and Hf 4f_{5/2}-N bonds, respectively. Similarly, N1s (Figure 3b) also exhibited two major peaks at binding energies of 399.7 eV and 402.7 eV, which originated from HfN and HfON bonds, respectively [46]. The HfON is formed due to the surface oxidation in air environment. Since the HfN film was 20 nm thick and conformally coated throughout the sample, there is no trace of Ti 2p signal, which is too deep for detection by the high-resolution XPS measurement.

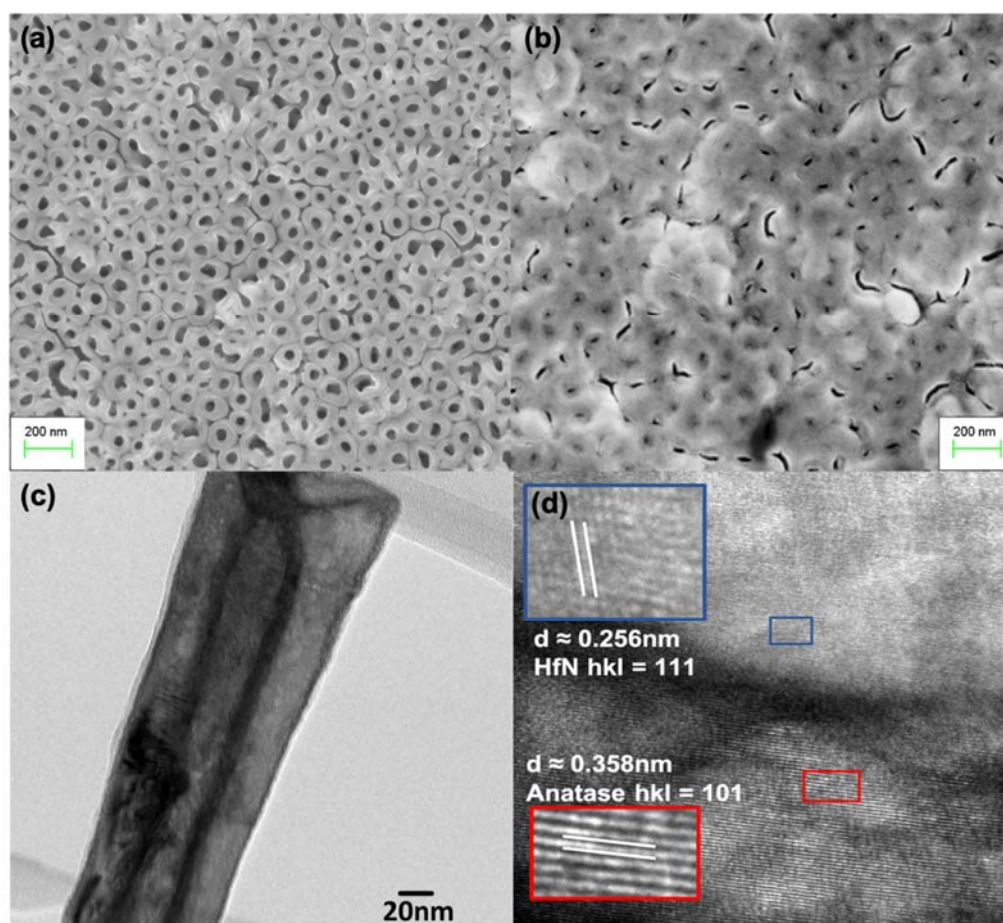


Figure 2. FESEM images for sample before and after ALD HfN coating, (a,b) are top view images before and after HfN coating; (c) HRTEM cross-section view image demonstrates the two layers constituting the core-shell nanotube morphology; (d) HRTEM image at the HfN and TiO₂ interface showing anatase TiO₂ (101) lattice fringes and HfN (111) lattice fringes.

The value of work function was calculated using the equation: $WF = 21.2 - E_{\text{cut-off}}$ in which $E_{\text{cut-off}}$ is the energy of emitted secondary electrons and 21.2 eV is according to the He laser UV light source. The secondary electron cut-off energy of this material is 18.4 eV (Figure 3c). According to the expression given before, the work function with respect to the vacuum level is 2.8 eV, which is up shifted by 1.5 eV from the normal WF value of 4.3 eV for anatase TiO₂ [24]. Additionally, the valence band maximum was calculated to be 5.21 eV (Figure 3d). Based on upward shifting and WF position, the material is electron degenerated after HfN coating due to its metallic property.

The phonon dispersion in HfN makes it an outstanding candidate for hot carrier-mediated photocatalysis. The constituent Hf and N atoms have a great difference in mass resulting in a large phonon gap between the optical and acoustic modes. In the Raman spectrum of the HfN-TNT sample (Figure 4a), the dominant four peaks are at 144 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g} and B_{1g}), and 639 cm⁻¹ (E_g) from anatase TiO₂. Further investigation focused on HfN phonon dispersion. Although there are some peaks that do not stand out from TiO₂ peaks, the signature Raman peaks for HfN phonon distribution are still noticeable. The peak representing the HfN transverse acoustic phonon mode is submerged in the TiO₂ E_g band at 140 cm⁻¹. Nevertheless, another signature peak for longitudinal acoustic phonons in the first-order acoustic band is observable at 199 cm⁻¹ in the spectrum. The first-order optical phonon band is well resolved at 540 cm⁻¹ and energetically distant from the first-order acoustic band. Other peaks, at 250 cm⁻¹, 350 cm⁻¹, 420 cm⁻¹, 800 cm⁻¹, and 1100 cm⁻¹, can be assigned to second-order transverse acoustic mode, the sum of transverse and longitudinal acoustic modes, the difference

between optical and acoustic modes, the sum of optical and acoustic modes, and second-order optical mode, respectively. It is worth noting that the first-order scattering peaks are not prominent in the Raman spectrum, which is due to the suppression of the first-order Raman effect by stoichiometric HfN with a low concentration of defects [47]. The source of first-order Raman scattering is usually attributed to N vacancies i.e., stoichiometric defects. The X-ray diffractogram (XRD) (Figure S1 in supporting information) indicates that HfN has a cubic fcc crystal structure, and the dominant (111) diffraction peak is a strong indication of stoichiometric HfN [48].

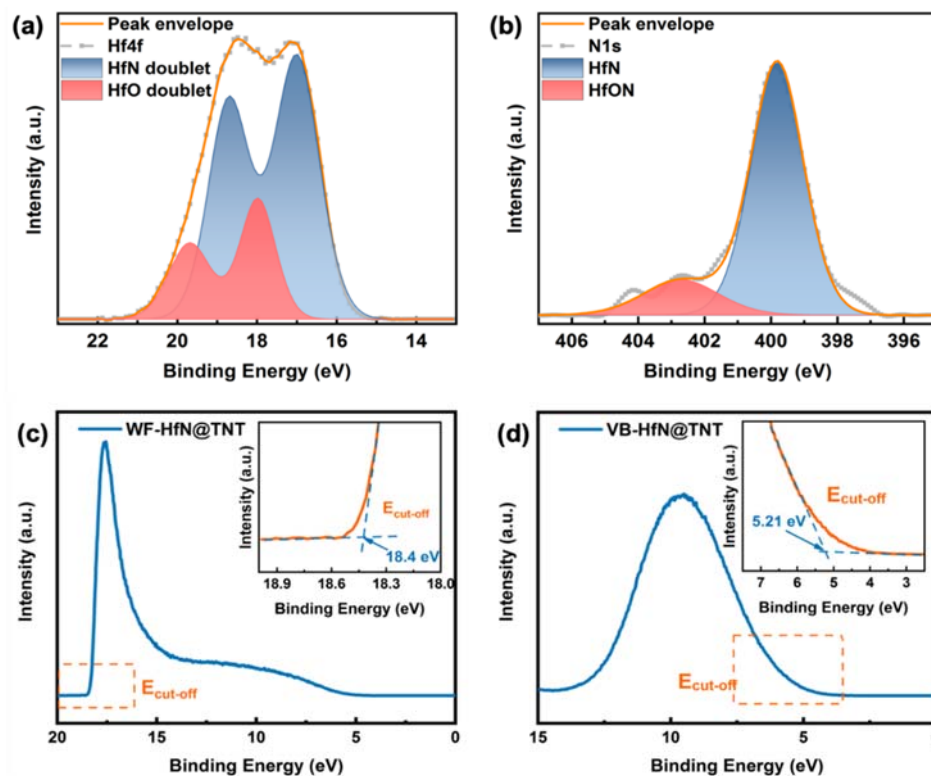


Figure 3. (a,b) Deconvoluted XPS spectra for Hf 4f and N 1s, respectively; (c,d) work function and valence band maximum with respect to vacuum level from ultraviolet photoelectron spectroscopy.

Klemens decay is the primary pathway for the loss of energy of optical phonons and is attenuated by a large phononic bandgap [49]. According to the Raman spectrum we presented in Figure 4a, the first-order acoustic and the first-order optical phonons were located at 140 cm^{-1} and 540 cm^{-1} respectively, meaning that the large energy difference between them prevents Klemens decay. This is a critical factor, because when the decay of optical phonons is suppressed, a phonon bottleneck is created and hot carriers tend to have a longer lifetime. HfN is a conductive ceramic with no electronic bandgap, which is a perfect characteristic for a hot carrier absorber [9]. The combination of these properties explains why we observed a small difference in photocurrent with and without a UV filter, obtaining a photocurrent response $1.74\text{ mA}\cdot\text{cm}^{-2}$ and $2.39\text{ mA}\cdot\text{cm}^{-2}$, respectively, at an applied bias of $+0.6\text{ V}$ during on-off cycles. Incident photons stimulate plasmon oscillations on the sample surface, which then decay into hot electron-hole pairs through Landau damping. Due to the presence of applied bias and relatively longer hot carrier lifetimes in HfN, the high-energy holes were pushed to the anode-electrolyte interface prior to thermalization and oxidized the OH^- ions in the water-based electrolyte to form O_2 . From a thermodynamic point of view, holes with energies higher than 1.23 eV are capable of splitting water. According to the AM 1.5 G solar spectral irradiance data, the percentage of photon flux (vs the cumulative flux of photons in sunlight) up to 750 nm (practical cut-off wavelength) is 31% with UV filter and 36% without UV filter, which

is in close agreement with the ratio of photocurrent we obtained with and without UV filter [50]. The conformal coating of HfN modified the optical properties of TiO₂ nanotubes (Figure 4b). The band edge shifted from 385 nm (anatase TiO₂) to 625 nm (HfN-TNT), thus enhancing visible light absorption. There also appeared a localized surface plasmon resonance (LSPR) peak centered at 720 nm with a *Q* factor equal to 0.95. Close to the LSPR peak, the maximum local electric field enhancement is observed at the HfN-TiO₂ interface (Figure S3 in Supporting Information). The peaks after 800 nm are due to the interference fringes that are well-known for TiO₂ nanotube arrays (Figure S4 in Supporting Information). It is worth noting that in the infrared regime, it displayed strongly increasing absorption, which indicated metal-like property due to high free carrier concentration.

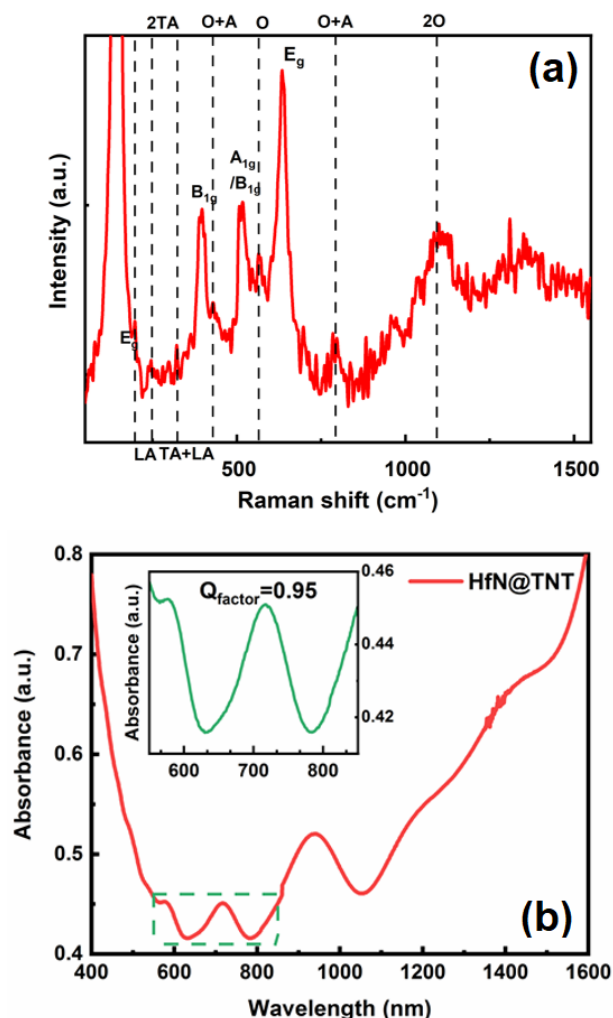


Figure 4. (a) Raman spectrum of HfN@TNT, TA stands for transverse acoustic mode, LA stands for longitudinal acoustic mode, O represents optical mode, and (b) UV-Vis absorption spectrum of HfN-TNT, and the inset is a zoom-in view of the localized surface plasmon resonance peak and its calculated quality factor.

2.3. Quantum Computation Results

The HOMO–LUMO plots (Figure 5) demonstrated that charge transfer excitation is prominent on HfN due to the fact that occupied and unoccupied regions are primarily composed of HfN orbitals, which is also supported by the projected density of states (PDOS) plot (Figure 6). Some tiny penetration of LUMO was observed in the close geometries, specifically in the case of TiO₂ (101) and the Hf-terminated HfN (111) system. These results indicate that the HfN planes are chemically more active compared to TiO₂. Figure 6a showed the PDOS of selected atoms in the HfN-TiO₂ system, where TiO₂ and HfN slabs

are kept far apart to ensure there is no interaction between them. As expected, the plot showed TiO_2 to be a wide bandgap *n*-type semiconductor whose valence and conduction bands are mostly composed of O-2p and Ti-3d states [51]. These figures also showed the electronic properties of HfN to be metallic with overlapped valence and conduction bands that are mostly composed of Hf d-states, which is consistent with earlier findings [8]. In the composite system, hot electron generation upon plasmon dephasing (Landau damping) within HfN is expected to be dominated by an intra-band transition involving the Hf d-orbital. These hot electrons can be injected into the TiO_2 d-orbital from HfN in an indirect plasmon-induced charge transfer excitation route.

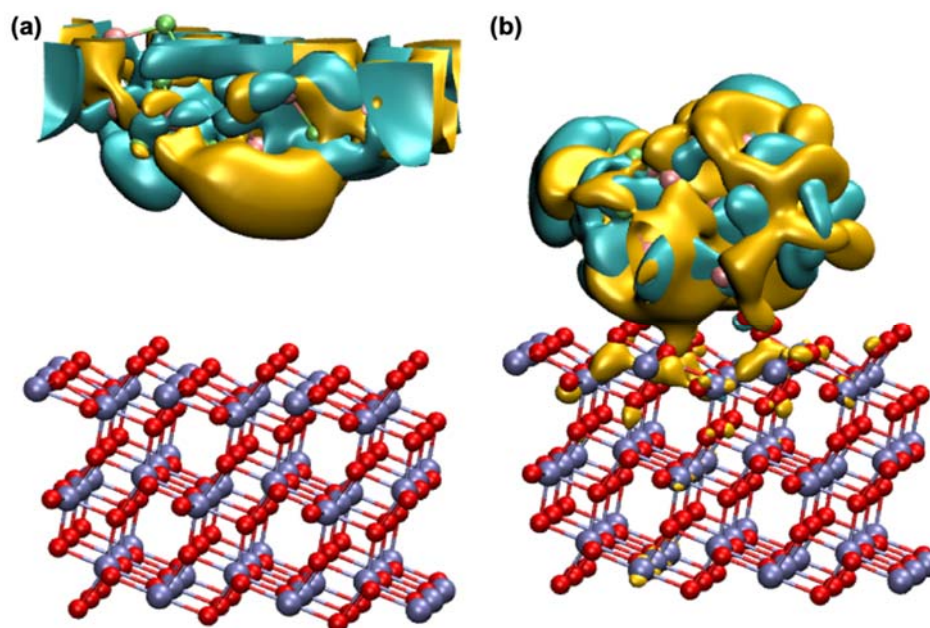


Figure 5. DFT optimized structures showing spatial positions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for TiO_2 (101) and HfN (111) are located at far (a) and close (b) configurations.

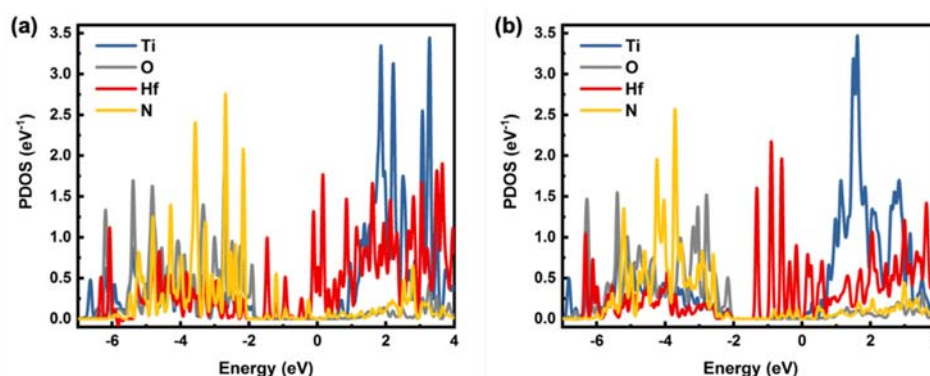


Figure 6. Projected density of states (PDOS) of selected atoms for HfN@ TiO_2 heterostructures in far and close configurations. TiO_2 (101) and HfN (111) with Hf-edge planes are located at far (a) and close (b) configurations.

Note that according to the density of states analysis, the plasmon-induced chemical interface damping (CID) is not expected to play any significant role in the heterostructures. In the CID mechanism, plasmon dephasing occurs at the plasmonic metal–semiconductor interfacial region, where dephasing and the subsequent generation of hot electrons occur directly in the newly formed interfacial hybridized orbitals [52,53]. According to Figure 6b, almost no indication of the formation of such preferred hybridized orbitals in the vicinity

of TiO₂ conduction band edge is evident due to a large discrepancy in the DOS intensity and associated orbital types. The overlap between relevant HfN orbitals with TiO₂ acceptor orbitals (in the conduction band region) was found to be inadequate for a CID-type mechanism to be dominant.

3. Materials and Methods

3.1. TiO₂ Nanotube Array Synthesis

The fluorine-doped tin oxide (FTO)-coated glasses were first washed by soap water and then ultrasonicated in deionized water, acetone, and methanol sequentially for 10 min each. After being dried under a nitrogen stream, the top 3 mm of each substrate was covered with Kapton tape, which was done to keep an FTO-exposed area for contact in later experiments. Then, the substrates were loaded into a direct current magnetron sputtering system. The sputtering chamber was first evacuated to 10⁻⁶ Torr and later filled with argon to achieve a working pressure of 1 mTorr. A Ti target with 99.99% purity was used to deposit a 500 nm thick, smooth Ti film on the substrates at room temperature while benefiting from the atomic peening mechanism [54]. After deposition, the substrates were cut into 2.5 cm × 3 cm pieces with edges protected by Kapton tape to limited high currents at edges and corners during the electrochemical anodization process. The samples were anodized at 40 V in a mixed ethylene glycol-based electrolyte containing 0.3wt % NH₄F and 4 v% deionized water. The electrochemical anodization was conducted in a two-electrode cell using the as-prepared sample as the working electrode and a 6 mm diameter graphite rod as the counter electrode with a 3 cm distance between the anode and cathode. The anodization process took around 10 min until the current began to rise and the substrate turned semi-translucent from metallic dark. After the anodization completed, the samples were rinsed with methanol and dried under nitrogen flow. To remove the debris that formed on the top of the TiO₂ nanotubes, a dry etching process was applied on synthesized samples using an Oxford PlasmaPro NGP80 Reactive Ion Etcher with SF₆ as the working gas at 20 mTorr and a forward power of 250 W for 200 s, and it was followed by O₂ plasma at 150 mTorr and a forward power of 225 W for 10 min. As-prepared samples were annealed in a three-zone tube furnace (STF55666C-1, Thermo Scientific Lindberg/Blue M), in which the temperature increased to 450 in 4 h and the dwell time was another 4 h.

3.2. ALD Deposition of Hafnium Nitride

HfN films were grown using a plasma-enhanced atomic layer deposition (PE-ALD) technique in a continuous flow ALD system (ALD150-LX, Kurt J. Lesker) at 1.01 Torr reactor pressure using remote inductively coupled plasma (13.56 MHz ICP, 0.6 kW, 60 sccm FG with 100 sccm Ar carrier). Tetrakis(dimethylamino)hafnium (TDMAHf) and forming gas (FG: 5% H₂ + 95% N₂) were the Hf-precursor and N-source, respectively. Process conditions for self-limiting HfN PEALD were characterized with in situ spectroscopic ellipsometry measurements (M2000DI, J. A. Woollam). Using growth-per-cycle (GPC) determined on a planar Si (111) substrate for PEALD cycle: 0.1 s TDMAHf pulse, 12 s post-precursor purge, 9 s FG plasma exposure, and 5 s post-plasma purge, 20 nm thick HfN film was grown on TiO₂ nanotube array structures in 300 cycles.

3.3. Materials Characterization

The optical spectra of the TiO₂@HfN nanotube arrays were measured in diffuse reflection mode using a UV-Vis-NIR spectrophotometer with an integrating sphere (Perkin Elmer Lambda 1050). The surface chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra instrument, and the survey scan is shown as Figure S2 in the supporting information. To obtain the electronic structure information and band edge energy, the work function spectrum and valence band spectrum were acquired using ultraviolet photoelectron spectroscopy (UPS) using a He laser UV source.

3.4. Photoelectrochemical Measurements

The measurement of photoelectrochemical water splitting was performed in a three-electrode system consisting of the as-prepared sample photoanode, Pt cathode, and Ag/AgCl reference electrode, in KOH electrolyte. A Newport Oriel solar simulator with Class A output was used to generate simulated solar light (AM 1.5G), and the power density upon the sample surface was 100 mW/cm². In order to measure the photocurrent response under visible light illumination, the simulated sun light (AM 1.5G) was filtered by a UV cut-off filter ($\lambda > 420$ nm). The photocurrent was obtained under linear sweep voltammetry mode, and the sweeping voltage was from -0.8 to $+1.0$ V versus Ag/AgCl. To investigate the photocurrent response of the sample at discrete wavelengths, near-monochromatic light LEDs were used to illuminate the sample at the power density of 10 mW/cm². The photocurrent response was collected at a constant potential of 0.3 V vs. Ag/AgCl.

3.5. DFT Modeling

Structures of HfN-TiO₂ composite systems for DFT calculations were built based on our collected X-ray diffractogram (XRD) data (shown in Figure S1 in the Supporting Information). The dominant TiO₂ anatase plane (101) was used to build composite systems with HfN (111) and (200) planes. While HfN (200) planes have both Hf and N atoms, HfN (111) planes have either Hf or N terminated atoms. Thus, we have considered three planes of HfN with the (10) plane of anatase TiO₂. All these three composite systems were constructed in both distant and proximate configurations. An OpenMx 3.9.2 (Open source package for Material eXplorer) package was used for density functional theory (DFT)-based quantum chemical calculations [55], where norm-conserving pseudopotentials [56] and pseudo-atomic localized basis functions [55] are implemented. The computational protocol involved two steps: geometry optimization followed by electronic property calculations using generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [57]. Spin-polarization with periodic boundary conditions was employed for all the calculations. Hubbard U-corrections (DFT+U) were considered in our DFT model for considering the computational errors associated with on-site Coulomb interactions. The Hubbard U-value for Ti 3d orbitals was considered to be 3.3 eV [58]. This Hubbard U-correction provides an additional on-site Coulomb interaction to compensate for the inaccurate description of self-interaction particularly in a partially occupied TiO₂ 3d state [59]. In this approach, the additional functions force the electrons of a particular orbital (for TiO₂ it is 3d orbital) to be more localized, thus ensuring the reproduction of experimental bandgaps [59]. The energy cut-off value was chosen to be 220 eV, while the threshold for convergence criterion for the self-consistent loop was set to be as small as 10⁻⁵. The Gaussian broadening method, with a broadening parameter of 0.08 eV, was used for the projected density of states (PDOS) plots. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were constructed using VMD (visual molecular dynamics) visualization software.

4. Conclusions

In this study, we reported a method for the fabrication of core–shell nanotube arrays consisting of a 20 nm ALD HfN shell and an anodic TiO₂ nanotube support layer. To the best of our knowledge, it is the first report using HfN for photoelectrochemical water splitting. We observed excellent full visible regime photoactivity up to 730 nm for water splitting, and based on our literature survey, the photocurrent density is superior to any plasmonic noble metal-enhanced TiO₂ based photoanodes. We consider the finding to be significant, as it demonstrated the far-reaching application potential of replacing active HER/HOR noble metals such as Au, Ag, Pt, Pd, etc. with lower-cost transition metal nitride ceramics. Moreover, the experimental results evidence two unique characteristics allowing a large population of long lifetime hot carriers, namely, a large bandgap between optical and acoustic phonon modes and the absence of an electronic bandgap, which particularly benefit hot carrier-based optoelectronic devices. It opens the window to a wide range of

applications that enhance their performance using plasmonic noble metals including but not limited to photocatalysis, photosynthesis, dye degradation, and hot carrier solar cells.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111374/s1>, Additional information on materials characterization and electromagnetic simulations, Figure S1: X-ray diffractogram of HfN-TiO₂ sample illustrating material components by separating signals, Figure S2: XPS survey scan of HfN@TiO₂ sample, Figure S3: Results of FDTD simulations of HfN-TiO₂ showing electric field intensities for (a) xy plane and (b) xz plane at the resonant wavelength of 650 nm, Figure S4: Optical extinction spectrum of a bare TiO₂ nanotube array, and Details related to the estimation of H₂ generation yields.

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