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COMMUNICATION

A Ta₃N₅/BN composite for enhanced photocatalytic water splittingYao Xu,^a Haifeng Wang,^a Jiaming Zhang,^a Zihao Zhang,^a Meng Liu,^a Xiaowei Tao,^a Jifang Zhang,^{*a} and Guijun Ma^{*a}Received 00th January 20xx,
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Narrow-bandgap Ta₃N₅ nanorods were intensely supported on BN substrate to produce a composite photocatalyst using a NH₄Cl-based vacuum nitridation. The charge separation efficiency of Ta₃N₅ was effectively enhanced due to electron transfer from Ta₃N₅ to the BN substrate, boosting both photocatalytic water oxidation and Z-scheme overall water splitting reactions.

Solar energy conversion into clean hydrogen resource through photocatalytic process is a promising strategy for sustainable energy systems.^{1, 2} However, the development of efficient photocatalyst is constrained by limitations in light harvesting, especially in the visible region that takes up 45% of solar spectrum³, and photon conversion efficiency, restrained by serious bulk and surface charge recombinations.⁴⁻⁸ Ta₃N₅ has emerged as a particularly promising photocatalyst due to its bandgap of only 2.1 eV. The conduct band minimum (CBM) and valence band maximum (VBM) of Ta₃N₅ are composed by Ta 5d and N 2p orbitals respectively, thermodynamically allowing for both photocatalytic and photoelectrochemical water redox reactions.^{9, 10} In 2002, Hitoki *et al.* reported photocatalytic water oxidation on Ta₃N₅ in presence of an electron acceptor.¹¹ However, subsequent studies have demonstrated that the performance of Ta₃N₅ is fundamentally limited by issues directly stemming from synthesis method. Specifically, Ta₃N₅ is typically prepared through a NH₃-based thermal nitridation process, which meets challenges including the formation of low-valence metal ions and O_N antisite defects within the crystal structure. These intrinsic defects act as recombination centers that severely suppress charge separation efficiency.^{12, 13} Furthermore, high temperature duration leads to particle agglomeration of the products, exacerbating charge

recombination issues. As a consequence of these synthesis-related challenges, Ta₃N₅ exhibits unsatisfactory photon conversion efficiencies in photocatalytic reactions.¹⁴⁻¹⁶

Nanostructural engineering, by precisely controlling the morphology and architecture of oxide precursors, has emerged as an effective strategy to improve charge separation efficiency in Ta₃N₅ photocatalysts by reducing charge transport distances and extending carrier lifetimes.¹⁷ Ma *et al.* applied Ta₂O₅ and Na₂CO₃ mixture to produce NaTaO₃/Ta₂O₅ composite, which was then used as precursor for thermal ammonolysis. This method suppressed Ta₃N₅ agglomeration and enhanced crystallinity.¹⁴ Wang *et al.* prepared Ta₂O₅ coated Pt/SiO₂ nanoparticles for the fabrication of hollow Ta₃N₅ nanoshell, subsequently loading CoO_x onto the outer surface of Ta₃N₅ and Pt left on inner shell after removing SiO₂.¹⁸ The nanoshell structure not only provided a structural framework for efficient charge transport but also facilitated directional carrier extraction by spatially separating reduction and oxidation cocatalysts, thus boosting charge separation. Wang *et al.* applied KTaO₃ as vaporous Ta resource to produce Ta₃N₅ nanorod single crystals and accelerate heat ammonium flow reduced the duration of nitridation process. The highly crystallized Ta₃N₅ nanorods with fewer defects realized one-step excitation overall water splitting reaction under visible light illumination.⁹ Nanostructured precursors enable controlled Ta₃N₅ particle morphology, effectively decreasing agglomeration and shortening carrier transport distances, while structuring catalyst/host interface promotes more efficient carrier transport, enhancing charge separation efficiency and thereby unlocking Ta₃N₅'s potential for photocatalysis.

Our group has developed a NH₄Cl-based vacuum nitridation method to synthesize transition metal (oxy)nitrides such as Ta₃N₅/Ta thin film,¹⁹ TaON powders²⁰ and ZnO:GaN nanoparticles.^{21, 22} For the preparation of the Ta₃N₅/Ta thin film,

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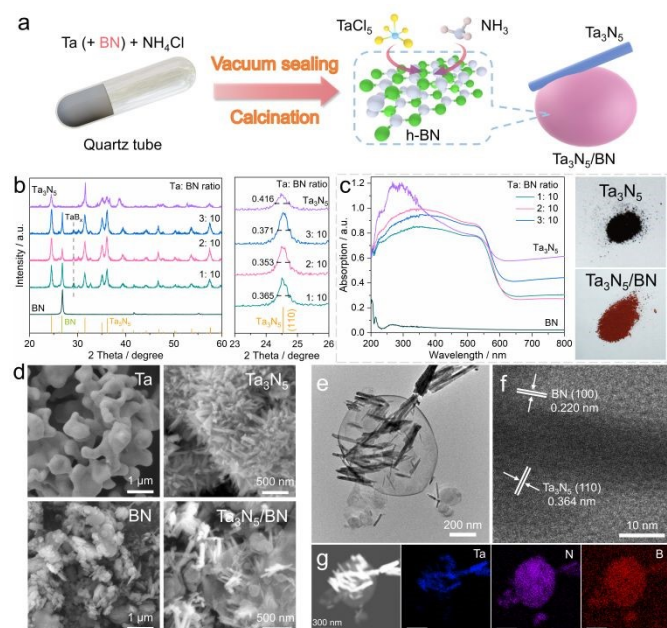


Figure 1. (a) Illustration of the synthesis of $\text{Ta}_3\text{N}_5/\text{BN}$ composite. (b) XRD patterns of BN precursor, bulk Ta_3N_5 , and the $\text{Ta}_3\text{N}_5/\text{BN}$ samples prepared from different Ta:BN ratios. (c) UV-vis DRS of BN, Ta_3N_5 , and $\text{Ta}_3\text{N}_5/\text{BN}$ powders as well as digital images of Ta_3N_5 and $\text{Ta}_3\text{N}_5/\text{BN}$ (Ta:BN = 2:10) samples. (d) SEM images of Ta and BN precursors and corresponding Ta_3N_5 and $\text{Ta}_3\text{N}_5/\text{BN}$ products. (e) TEM, (f) HRTEM, (g) dark field image and EDS mapping images of $\text{Ta}_3\text{N}_5/\text{BN}$ (Ta:BN = 2:10) sample. The referenced patterns of BN and Ta_3N_5 in (b) are ICDD-00-045-1171 and ICDD-04-004-4564, respectively.

only Ta wafer and NH_4Cl are used as precursors. Upon heating, in the first step, NH_3 and HCl are produced from the decomposition of NH_4Cl . The metallic Ta reacts with HCl to produce a gaseous TaCl_5 intermediate, which subsequently reacts with NH_3 to form Ta_3N_5 particles on the surface of Ta plate. The high permeability of gaseous TaCl_5 and NH_3 reactants not only leads to a fast crystallization of the solid product, but also prevents Ta_3N_5 from forming reduced Ta species by limited exposure to NH_3 atmosphere.

Herein, we introduced a two-dimensional BN as substrate for growth of Ta_3N_5 nanoparticles in the NH_4Cl -based nitridation process. The involvement of BN in precursor led to improved crystallinity and dispersion of the Ta_3N_5 particles. Reductive photodeposition of Ag and Rh suggested that electrons were transferred from Ta_3N_5 to BN under irradiation. Such directional charge migration greatly enhanced photocatalytic activities of Ta_3N_5 for water splitting, highlighting the benefits of photocatalyst-substrate interaction.

The Ta_3N_5 bulk and $\text{Ta}_3\text{N}_5/\text{BN}$ composite were synthesized by vacuum sealing a mixture of NH_4Cl and metallic Ta powders in a quartz tube with or without adding BN (Fig. 1a with details shown in Supporting Information). For $\text{Ta}_3\text{N}_5/\text{BN}$, the atomic ratios of Ta:BN were set as 1:10, 2:10 and 3:10, respectively. Fig. 1b displays the X-ray diffraction (XRD) patterns of the powders prepared from different Ta:BN ratios. All the BN-containing samples exhibit patterns of mixed BN and Ta_3N_5 peaks, with a weak signal at $\sim 29^\circ$ assigning to TaB_x impurities. The majority peaks of $\text{Ta}_3\text{N}_5/\text{BN}$ are consistent with standard Ta_3N_5 patterns, indicating the high purity of Ta_3N_5 in obtained samples. No

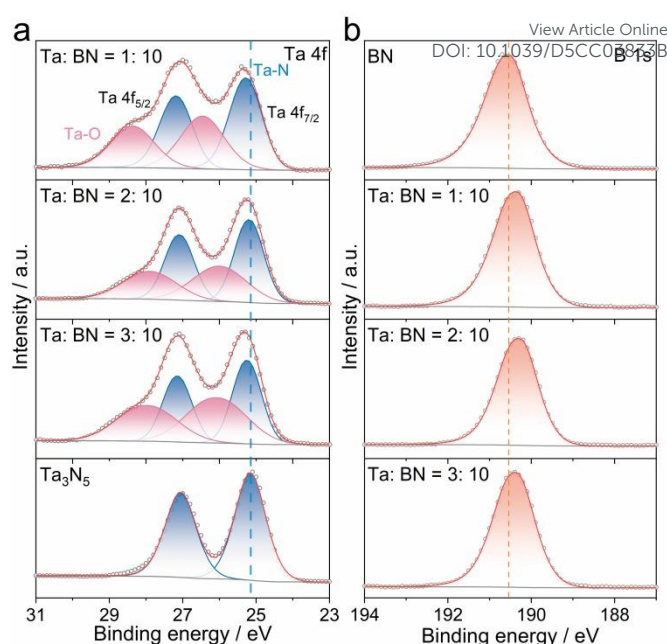


Figure 2. XPS of the $\text{Ta}_3\text{N}_5/\text{BN}$ samples prepared from different precursor ratios with including Ta_3N_5 , BN for reference. (a) Ta 4f, and (b) B 1s spectra.

signals of metallic Ta are observed in the products. Additionally, the full width half maximum (FWHM) of Ta_3N_5 (110) diffraction peaks in $\text{Ta}_3\text{N}_5/\text{BN}$ samples are lower than that of Ta_3N_5 , indicating enhanced crystallinity of Ta_3N_5 when BN is presented during synthesis. Fig. 1c shows the UV-vis diffuse reflectance spectroscopy (DRS) of BN, Ta_3N_5 and $\text{Ta}_3\text{N}_5/\text{BN}$ powders. The BN precursor exhibits negligible UV-visible light absorption due to its wide bandgap of 5.1 eV. Ta_3N_5 reference powder shows a broad absorption up to 600 nm corresponding to its bandgap (2.1 eV). The observed dark brown color, as opposed to dark red, can be attributed to elevated absorption in the near-infrared region. All $\text{Ta}_3\text{N}_5/\text{BN}$ samples exhibit smooth band-to-band absorption features typical of Ta_3N_5 , revealing that optical property of Ta_3N_5 is not changed with the introduction of BN in precursor as corroborated by the Tauc plots in Fig. S1. Compared to Ta_3N_5 , the relatively lower background levels above 600 nm for the $\text{Ta}_3\text{N}_5/\text{BN}$ samples suggest less absorption associated with intragap defect states. Notably, the Ta:BN = 2:10 sample achieves the strongest light absorption, showing that photon absorption is not linearly increased with higher Ta ratio in precursor.

Scanning electron microscopy (SEM) images (Fig. 1d) display morphology of the precursors and nitridation products. Without incorporating BN during nitridation, large Ta precursor particles are converted into aggregated Ta_3N_5 nanorods. In the presence of BN, the nitridation products show more uniformly distributed and well-isolated Ta_3N_5 particles dispersed on the BN substrate. SEM images of different $\text{Ta}_3\text{N}_5/\text{BN}$ samples (Fig. S2) in back scattered electron (BSE) mode show that the dispersity of Ta_3N_5 nanorods in the Ta:BN = 2:10 sample are higher than that in the 1:10 and 3:10 samples. It demonstrates that Ta content can effectively impacts on the growth of Ta_3N_5 particles, highlighting



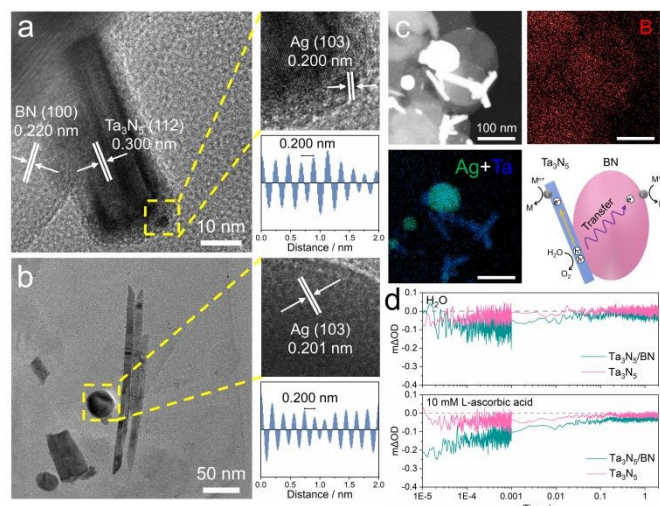


Figure 3. HRTEM images and lattice fringe distances of Ag particles loaded on (a) Ta₃N₅ and (b) BN in Ta₃N₅/BN particles. (c) Dark field image, EDS mappings and structure diagram of Ta₃N₅/BN sample loaded with Ag. (d) Transient absorption spectrum for Ta₃N₅ and Ta₃N₅/BN in water without (top panel) or with L-ascorbic acid (bottom panel). The pump and probe lights in (d) are 355 and 580 nm, respectively. The Ta₃N₅/BN sample is prepared from a Ta:BN = 2:10 ratio.

the NH₄Cl-based vacuum nitridation a potential method for constructing regulated nanostructures. Transmission electron microscopy (TEM) image of Ta:BN = 2:10 sample (Fig. 1e) shows that Ta₃N₅ nanorods with lengths around hundreds of nanometers lying on BN substrate. The BN structure remains unchanged after the high-temperature nitridation. The TEM image clearly demonstrates that Ta₃N₅ particles in obtained samples adopt a typical nanorod morphology, which is similar to those Ta₃N₅ particles prepared directly from TaCl₅ and NH₃ precursors.²³ High resolution TEM (HRTEM) image in Fig. 1f exhibits the interface of Ta₃N₅ and BN particles. The close stacking of 0.364 nm lattice fringes assigning to (110) facet of Ta₃N₅ and 0.220 nm lattice fringes assigning to BN (100) facet suggests the growth of Ta₃N₅ on BN substrate. Fig. 1g shows the TEM dark field image and energy dispersive X-ray spectroscopy (EDS) of Ta:BN = 2:10 sample. The overlapped N and Ta signals further confirm the nanorod morphology of Ta₃N₅ on BN substrate.

XPS analysis was carried out on Ta₃N₅, BN and Ta₃N₅/BN particles. The well-defined double peaks at 25.2 and 27.1 eV (Fig. 2a) assigning to Ta 4f_{7/2} and 4f_{5/2} in Ta₃N₅ reveal that the NH₄Cl-based nitridation suppresses the formation of reduced Ta species. For Ta₃N₅/BN particles, additional double peaks are observed at high field shift, which is supposed to be TaO_x impurities.²⁴ O 1s spectrum (Fig. S3) reveals the existence of crystalline O species in Ta₃N₅ and Ta₃N₅/BN, suggesting surface coverage of those TaO_x species. Besides, compared with Ta₃N₅, a slightly higher binding energy of Ta⁵⁺ signals in Ta-N of Ta₃N₅/BN samples reflects a possible electron transfer from Ta₃N₅ to BN. Relative to BN, the lower shift in B 1s binding energy for Ta₃N₅/BN samples also suggests an interfacial electron transfer between two components (Fig. 2b).

To verify electron transfer between Ta₃N₅ and BN under illumination, visible light-driven photoreduction of Ag⁺ ions was

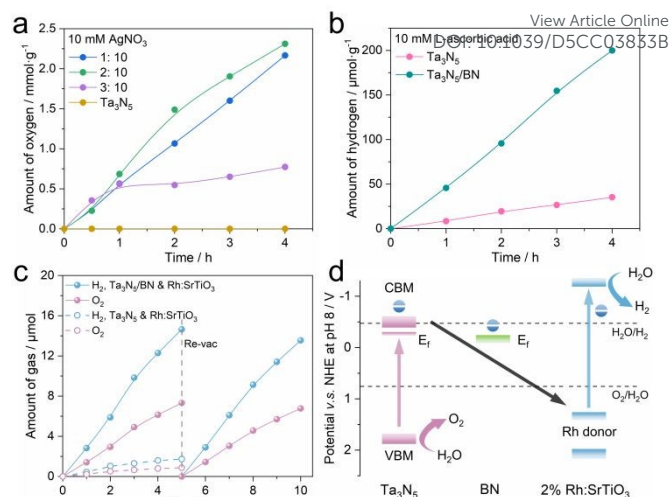


Figure 4. (a) Time profiles of photocatalytic OER on Ta₃N₅/BN and bulk Ta₃N₅ samples in AgNO₃ reagent. (b) HER activities of Ta₃N₅/BN and Ta₃N₅ in L-ascorbic acid reagent. (c) H₂ and O₂ production from physical oscillation between Ta₃N₅/BN and 2% Rh: SrTiO₃ at pH 5. (d) Diagram of Z-scheme electron transfer between Ta₃N₅/BN and Rh: SrTiO₃. The Ta₃N₅/BN in (b) and (c) are prepared from a Ta:BN = 2:10 ratio and each assessment applied 30 mg catalyst. 0.75 wt% IrO₂ and 1 wt% Pt was loaded as cocatalyst for OER and HER, respectively.

Ag particles are loaded on the Ta₃N₅/BN composite photocatalyst. The 0.200 nm lattice fringes attributing to Ag (103) facet are observed on both BN and Ta₃N₅ particles. The EDS mappings in Fig. 3c clearly distinguishes the Ag nanoparticles loaded away from Ta₃N₅ nanorods. Considering that BN barely absorbs visible light, it indicates that photogenerated electrons are partially transferred from Ta₃N₅ to BN, as illustrated in structure diagram of Fig. 3c. As a further evidence, by using Rh³⁺ as a precursor, Rh nanoparticles can also be reductively photodeposited on the BN substrate (Fig. S4). Mott-Schottky analysis and valence spectra (Fig. S5) reveal that the Fermi level of BN is closely aligned with that of Ta₃N₅. Such energetic alignment is beneficial for electron transfer from Ta₃N₅ to BN.

Transient absorption spectroscopy was employed to investigate the electron transfer from Ta₃N₅ to BN under light excitation and in solution. The pump and probe lights were set at 355 and 580 nm, respectively. For BN alone (Fig. S6), no meaningful transient absorption signal is observed as its band gap exceeds the pump light wavelength. On the other hand, both Ta₃N₅ and Ta₃N₅/BN show a weak negative absorption at 580 nm (Fig. 3d). To assign this signal, L-ascorbic acid is added as a hole scavenger. Here, the intensity of the negative absorption increases for both samples, confirming that such signal is associated with photogenerated electrons. It is worth noting that the negative absorption for Ta₃N₅/BN is significantly stronger than that for Ta₃N₅, indicating superior charge carrier separation in the former sample.

The catalyst-substrate electron transfer in Ta₃N₅/BN is supposed to promote its photocatalytic performance via improving electron-hole separation. Fig. 4a displays the activities of photocatalytic oxygen evolution reaction (OER) on Ta₃N₅ or Ta₃N₅/BN in presence of AgNO₃ as an electron scavenger. An IrO₂ species is loaded on the catalysts to assist



the OER process (Fig. S7). The Ta₃N₅ nanorods barely produce oxygen due to rapid passivation by Ag coverage on its active sites.²³ However, Ta₃N₅/BN exhibit linear oxygen evolution in the early stages, revealing that electron interaction slows down the Ag passivation and preserves photocatalytic activity. Among Ta₃N₅/BN products, the Ta:BN = 2:10 sample has the highest water oxidation rate. It is likely due to better photon absorption (Fig. 1c) and the more uniform distribution of Ta₃N₅ nanorods on BN substrate (Fig. S2) for this sample.

Fig. 4b displays photocatalytic hydrogen evolution (HER) on Ta₃N₅/BN (Ta:BN = 2:10) and Ta₃N₅ assisted with L-ascorbic acid as a hole sacrificial reagent. Pt (1 wt%) is optimized as the HER cocatalyst (Fig. S7). The Ta₃N₅/BN composite structure also shows a considerably enhanced hydrogen evolution rate compared with Ta₃N₅ nanorods, despite a much lower HER rate compared to OER. This highlights the thermodynamic limitations of Ta₃N₅/BN for proton reduction (Fig. S8). To break such limitation, Fig. 4c displays a Z-scheme overall water splitting reaction by physical collision between Ta₃N₅/BN and Rh doped SrTiO₃ (Rh:SrTiO₃) particles. Under visible light illumination, stoichiometric hydrogen and oxygen evolution over 10 h is realized for Ta₃N₅/BN, while the Ta₃N₅ exhibits significantly lower activity. Fig. 4d represents the band structure of Ta₃N₅/BN and Rh:SrTiO₃ determined from Mott-Schottky and bandgap assessment in Fig. S9. It is obvious that transfer of photogenerated electrons from Ta₃N₅ to BN favors the Z-scheme electron transfer pathway, effectively overcoming the insufficient reduction driving force of Ta₃N₅/BN.

In summary, a Ta₃N₅/BN composite photocatalyst is synthesized *via* the NH₄Cl-based vacuum nitridation process. The Ta₃N₅ component exhibits highly crystallized nanorod morphology during growth on the BN substrate. Photodeposition of Ag metal, chemical state analysis and carrier dynamics assessment confirm electron transfer between Ta₃N₅ and BN. Enhanced photocatalytic performance in water splitting emphasizes the promotion of charge separation efficiency by electron interaction of catalyst/substrate interface. Our work not only provides a new method for synthesizing highly crystallized Ta₃N₅ nanorods but also demonstrates an efficient composite structure for enhancing the photocatalytic performance of this promising photocatalyst.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.

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Data availability

The data supporting this article have been included as part of the ESI.