Achievement of visible-light-driven Z-scheme overall water splitting using barium-modified Ta$_3$N$_5$ as a H$_2$-evolving photocatalyst†

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Ta$_3$N$_5$ is one of the most promising photocatalyst candidates for solar water splitting, but it still remains challenging to achieve overall water splitting via Ta$_3$N$_5$-based photocatalysts regardless of whether it uses a one step or two step method. Here we will address the relatively poor photocatalytic proton reduction of Ta$_3$N$_5$ with an effort for the promotion of charge separation via barium modification. One-pot nitridation of barium nitrate-impregnated Ta$_2$O$_5$ precursor was adopted here for the synthesis of Ta$_3$N$_5$ accompanied with the creation of a Ta$_3$N$_5$/BaTaO$_2$N heterostructure and surface passivation. Due to the synergetic effect of the improved interfacial charge separation and the decreased defect density, the photocatalytic H$_2$ evolution rate of barium-modified Ta$_3$N$_5$ is effectively promoted. Encouraged by this, a visible-light-driven Z-scheme overall water splitting system was successfully constructed by using the barium-modified Ta$_3$N$_5$ as a H$_2$-evolving photocatalyst, together with a PtO/WO$_3$ and IO$_3^-$/I$^-$ pair as an O$_2$-evolving photocatalyst and a redox mediator, respectively.

Introduction

Semiconductor-based photocatalytic overall water splitting for hydrogen production is an ideal way to convert solar energy to chemical energy and has inspired extensive interest in the past few decades.¹–³ Towards this, hundreds of semiconductors have been reported for potential solar water splitting, but most of them are only active under UV light irradiation.⁶–¹⁰ To achieve highly efficient solar-to-chemical energy conversion, overall water splitting on photocatalysts harvesting visible light with longer wavelength is desirable. To date, however, the number of wide visible-light-driven overall water splitting systems, regardless of whether they use a one step or two step method, is limited.⁵,¹³–¹⁸

Tantalum nitride (Ta$_3$N$_5$), with a theoretical solar-to-chemical energy conversion efficiency of 15.9%, is one of the most promising candidates for solar water splitting, considering its matched band edge positions (conduction band and valence band edges at ca. −0.4 V and +1.7 V vs. NHE, respectively, at pH = 0), wide visible light harvesting ability (up to 600 nm) and good photo-stability.¹⁹–³⁷ It was first synthesized in 1973,³⁸ but was not found to be active for the photocatalytic water splitting reaction until 2002.¹⁹ Afterwards, Ta$_3$N$_5$ has been widely investigated for water splitting in terms of particulate photocatalysts³⁹–⁴³ and photoanodes.³⁶–⁴¹

The increasing research interest and efforts have greatly promoted the water oxidation performance of Ta$_3$N$_5$ for both particulate photocatalyst and photoanode systems. For example, Li et al. fabricated a 1D Ta$_3$N$_5$ nanorod photoanode to achieve a STH of 1.5%.³⁹ Liu et al. achieved Ta$_3$N$_5$ photoanode stability for hours²⁷ and obtained nearly close to the theoretical photocurrent at a potential of 1.23 V vs. RHE under AM 1.5G simulated sunlight.³¹ Chen et al. reported that the apparent quantum efficiency of the photocatalytic water oxidation activity of the Ta$_3$N$_5$-based particulate photocatalyst can reach 11.3% at 500–600 nm via an interface engineering strategy.²⁴ Compared to the water oxidation, however, the activity of photocatalytic proton reduction from water is much lower or even undetectable in most cases, even though extensive investigations such as forming polymorphic macroporous Ta$_3$N$_5$, reducing the particle size through templates (i.e. SiO$_2$, C$_3$N$_4$) and surface modification have been made.²³–³⁷ As a result of the poor proton reduction ability, Z-scheme overall water splitting using particulate Ta$_3$N$_5$ as a H$_2$-evolving photocatalyst is still not reported.

Fabricating nanocomposites with another semiconductor to form heterostructures has been extensively adopted for the promotion of photocatalytic performances.³⁶,²⁹–⁴¹ A heterostructure can create external bias through interfacial junctions to spatially separate the photogenerated electrons and holes.
However, it should be pointed out that most of the (oxy)nitrile photocatalysts are thermally instable in air, so the fabrication of a heterostructure for (oxy)nitrile commonly confronts technical challenges, rendering feasible examples very limited.16

In this work, a barium modification strategy is introduced to address the relatively poor photocatalytic proton reduction activity of Ta3N5 under visible light irradiation. A simple one-pot nitridation route was adopted for the synthesis of pristine Ta3N5 and barium-modified Ta3N5, in which a barium nitrates-impregnated Ta2O5 was used as a precursor. It is found that some Ba2+ ions could be doped into Ta3N5 to decrease its defect density. On the other hand, excessive Ba2+ ions will produce BaTaO2N in situ on the surface of Ta3N5 to create a Ta3N5/BaTaO2N heterostructure. As a result, the photogenerated carrier separation efficiency of Ta3N5 can be promoted after the barium modification, causing an effectively enhanced H2 evolution rate in the presence of methanol. Finally, the first example of a visible-light-driven photocatalytic Z-scheme overall water splitting system using the modified Ta3N5 as a H2-evolving photocatalyst was successfully constructed.

Experimental
Materials and reagents

For the preparation of Ba(n)-Ta3N5 samples, Ta3O5 (99.99%, Amresco Chemical), and Ba(NO3)2 (99.5%, Sinopharm Chemical) were used. WO3 (99.99%, High Purity Chemical) was used as a water oxidation photocatalyst. H2PtCl6·6H2O (99.5%, Sinopharm Chemical) was employed as the precursor for the reduction cocatalyst. CH3OH (99.5%, Sinopharm Chemical) and NaI (99.5%, Guangfu Chemical) were used as sacrificial electron donors. L2O3 (99.95%, Sinopharm Chemical) was applied as a pH buffer agent. All chemicals were used as purchased without further purification.

Preparation of Ba(n)-Ta3N5 samples

Typically, Ta3O5 powder was impregnated in the Ba(NO3)2 aqueous solution with a calculated molar ratio of Ba/Ta, and the dried mixture was then annealed in air at 1073 K for 2 h. The as-prepared powder was treated with “one-pot” nitridation under ammonia flow (250 mL min⁻¹) at 1223 K for 20 h. The as-obtained samples are correspondingly denoted as Ba(n)-Ta3N5, where “n” stands for the molar ratio of Ba/Ta and when n = 1 it stands for BaTaO2N. As a comparison, the pure phase of Ta3N5 and BaTaO2N powder was mechanically mixed at a Ba/Ta molar ratio of 0.3, which is denoted as Ta3N5/BaTaO2N (0.3)-mix.

Deposition of cocatalysts

0.2 g of the as-obtained sample was dispersed in a calculated amount of H2PtCl6 aqueous solution, and sonicated for ca. 5 min. After the solution was completely evaporated in a water bath at 353 K, the resulting powder was collected and reduced at 473 K for 1 h under a flow of 5% H2/Ar (200 mL min⁻¹). As for the deposition of PtOx on the surface of WO3 for water oxidation, typically, 0.3 g of WO3 was annealed in the air at 773 K for 2 h, and then 0.2 g of the annealed sample was immersed in a calculated amount of H2PtCl6 aqueous solution with sonication for ca. 5 min. After complete evaporation in a water bath at 353 K, the resulting powder was collected and annealed in air at 798 K for 0.5 h.

Electrochemical analysis

For the Mott–Schottky (M–S) measurement, Ta3N5 and BaTaO2N powder were deposited on FTO conducting glass via electrophoretic deposition (EPD). Typically, the powder samples (50 mg) and iodine (20 mg) were dispersed in acetone solution (50 mL), and continuously sonicated for 10 min. Afterwards, the FTO electrode was immersed, parallel to another FTO electrode, with a distance of about 1 cm. The duration time was 1 min with 20 V and 1 A applied using a potentiostat (ITECH IT6834), and then the prepared electrodes were calcined under an ammonia flow (250 mL min⁻¹) at 723 K for 0.5 h.

The M–S measurement was carried out using a Princeton Applied Research PARSTAT 2273, using 0.5 M Na2SO4 aqueous solution as electrolyte with a pH value of 8.5 adjusted using NaOH. The frequency was 1 kHz.

Characterizations of catalysts

XRD measurements were carried out using a Rigaku D/Max-2500/PC powder diffractometer (Cu Kα radiation) with an operating voltage of 40 kV and an operating current of 200 mA. A scan rate of 5° min⁻¹ was applied in the range of 10–60°. UV-vis diffuse reflectance spectra (DRS) were recorded using a UV-vis spectrophotometer (JASCO V-550) equipped with an integrating sphere, and BaSO4 powder was used as the reference for the baseline correction. The morphologies and particle sizes were examined using field emission scanning electron microscopy (FESEM; S-5500, Hitachi). High-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai G2 F30 S-Twin (FEI Company) with an accelerating voltage of 300 kV. For the time-resolved IR spectroscopic study, the photocatalyst was fixed on a CaF2 plate at a density of 2 mg cm⁻² and placed in a gas cell evacuated at 10⁻⁵ Torr. The Brunauer–Emmett–Teller (BET) surface area was measured at 77 K using a Micromeritics ASAP 2000 adsorption analyzer. Transient IR absorption signals were recorded on a Nicolet 870 FTIR spectrometer with a MCT detector. A pulse laser at 355 nm (1 Hz, 3 mJ per pulse) was used to excite the samples. The width of the laser pulse was 6–8 ns and no deconvolution on the data was carried out.

Photocatalytic reactions

Photocatalytic reactions were carried out in a Pyrex top-irradiation type reaction vessel connected to a closed gas circulation system. Before photoirradiation, the reaction system was evacuated to completely remove air, and then irradiated from the top side using a 300 W xenon lamp with a filtration mirror equipped with an optical filter (Hoya, L-42; λ > 420 nm) to cut off the ultraviolet light. A flow of cooling water was used to keep the reaction suspension at room temperature. Gas chromatography (Agilent; GC-7890A, MS-5A column, TCD, Ar carrier) was used to
analyze the evolved gases. The pH value before and after the photocatalytic overall water splitting reaction was similarly kept at ca. 6.

Measurement of AQE

The AQE measurement was carried out using a Pyrex top-irradiation-type reaction vessel and a 300 W xenon lamp fitted with a 420 nm band-pass filter. The number of photons reaching the reaction solution was measured using a calibrated Si photodiode (LS-100, EKO Instruments Co., LTD.), and the AQE (φ) was calculated according to the following equation:

$$\phi(\%) = \left(\frac{AR}{I}\right) \times 100$$

where A represents a coefficient (4 for H₂ evolution; 8 for O₂ evolution), R represents the evolution rate of H₂ or O₂ in the initial one hour irradiation and I represents the absorption rate of incident photons. It was assumed that all incident photons were absorbed by the suspension. The total number of incident photons at a wavelength of 420 nm was measured to be $4.76 \times 10^{20}$ photons per h.

Results and discussion

Fig. 1A shows XRD patterns of the Ba(n)–Ta₃N₅ samples (n = 0–1), in which all of them exhibit a well-crystallized feature. When the Ba/Ta molar ratio is below 0.03, only diffraction peaks assigned to a single phase of Ta₃N₅ are observed. With a further enhanced molar ratio of Ba/Ta, additional diffraction peaks attributed to BaTaO₂N appear, the intensities of which are continuously increased. Compared with the diffraction peaks of the unmodified Ta₃N₅ sample, a little shift in the diffraction peaks toward a lower angle is observed for the barium-modified Ta₃N₅ samples (Fig. S1†). This demonstrates that the six-coordinated Ba²⁺ may be partly doped into Ta₃N₅ to substitute the Ta⁵⁺ sites, similar to the previous report.²⁰

Fig. 1B shows the UV-vis spectra of the Ba(n)–Ta₃N₅ samples, in which all of the samples similarly exhibit a wide visible light absorption at around 600 nm. The absorption edge is continuously red-shifted with the increasing molar ratio of Ba/Ta, which should be the result of the formed BaTaO₂N species. Compared to the pristine Ta₃N₅ sample, the absorption background originating from the formation of reduced tantalum species (e.g., Ta⁴⁺ and Ta¹⁴⁻)³¹,³² on the Ba(n)–Ta₃N₅ samples undergoes an initial decrease and a subsequent increase with the enhancing molar ratio of Ba/Ta. To understand the UV-Vis results, a single phase of BaTaO₂N was prepared via the same preparation procedure. As shown in Fig. 1B, the absorption edge of BaTaO₂N is at about 660 nm, and its absorption background is the highest among all of the Ta₃N₅-based samples. It is generally understood that the UV-vis absorption background of the mechanically mixed sample containing two phases should be located between that of the corresponding single phases. That is to say, if the Ba(n)–Ta₃N₅ samples are just a simple mixture of Ta₃N₅ and BaTaO₂N, the absorption background of the Ba[n]–Ta₃N₅ samples will lie between those of the Ta₃N₅ and BaTaO₂N. In this work, however, the samples with a molar ratio of Ba/Ta below 0.3 exhibit much lower absorption backgrounds than those of both Ta₃N₅ and BaTaO₂N. This means that the as obtained Ba(n)–Ta₃N₅ samples do not exist as a simple mixture of Ta₃N₅ and BaTaO₂N, but exist as a nanocomposite. In consideration of that, here the Ta₃N₅ and BaTaO₂N phases are one-pot synthesized, thus the BaTaO₂N is expected to be formed in situ on the surface of Ta₃N₅ to partly eliminate the surface dangling bonds of Ta₃N₅. On the other hand, the partial barium ions are doped into Ta₃N₅ to inhibit the defect formation. Both of them cause the decrease of defect density. However, it needs to be pointed out that BaTaO₂N itself exhibits the highest defect density among all of the samples. Thus, when the molar ratio of Ba/Ta is excessively enhanced, the defect density of the Ba(n)–Ta₃N₅ sample will become higher.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Structural characterizations of typical Ba(n)–Ta₃N₅ samples (n = 0–1); (A) XRD patterns and (B) UV-vis spectra. “n” stands for the molar ratio of Ba/Ta. The inset figure is enlarged for the wavelength range of 500–800 nm.
In Fig. 2f, the Ta element originating from both Ta$_3$N$_5$ and Ba(0.3)TaO$_2$N, while the locations with Ta element mapping but a shortage of Ba element mapping stand for the Ta$_3$N$_5$ species. The formation of the Ta$_3$N$_5$/BaTaO$_2$N nanocomposite can be further supported by the elemental mapping results (Fig. 2e).

In Fig. 2f, the Ta element originating from both Ta$_3$N$_5$ and BaTaO$_2$N is dispersed everywhere, while the Ba element that can only result from BaTaO$_2$N is only found in some specific places (Fig. 2g). This can be easily understood to show that the places with Ba element mapping mainly reveal the existence of BaTaO$_2$N, while the locations with Ta element mapping but a shortage of Ba element mapping stand for the Ta$_3$N$_5$ species. Based on the elemental mapping images, we can reasonably give a simulation of the composite state of Ta$_3$N$_5$ and BaTaO$_2$N for the Ba(0.3)–Ta$_3$N$_5$ sample (Fig. 2h). For comparison, the element mapping results of mechanically mixed Ta$_3$N$_5$ and BaTaO$_2$N (Ta$_3$N$_5$/BaTaO$_2$N (0.3-mix)) are given in Fig. S2,$^\dagger$ from which the Ta$_3$N$_5$ and BaTaO$_2$N phases are mainly separated, different from that of the Ba(0.3)–Ta$_3$N$_5$ sample. It needs to be pointed out that the composite of Ta$_3$N$_5$ and BaTaO$_2$N does not exist in a core–shell configuration. In addition, the surface areas of the Ba(n)–Ta$_3$N$_5$ samples are similar to that of BaTaO$_2$N (7 m$^2$ g$^{-1}$) but a little lower than that of Ta$_3$N$_5$ (9 m$^2$ g$^{-1}$), which should result from their shortage of porous structure (Table 1).

To further confirm the formation of the nanocomposite, we carried out a (HR)TEM characterization. Fig. 3 gives the representative images of the Ba(0.3)–Ta$_3$N$_5$ sample, in which the interface of the nanocomposite can be clearly observed. As shown in Fig. 3, the obvious lattice fringes indicate that the sample synthesized in this work is well-crystallized, in accordance with the XRD patterns (Fig. 1A). Based on the measurement of lattice distance, we can easily judge the BaTaO$_2$N and Ta$_3$N$_5$ phases. Strikingly, the interfacial contact between BaTaO$_2$N and Ta$_3$N$_5$ is very intimate, revealing the formation of the nanocomposite. The formation of the intimate interface should originate from the one-pot high temperature route and their similar Ta-based octahedron units. In this case, BaTaO$_2$N is expected to be formed in situ on the surface of Ta$_3$N$_5$ during the one-pot nitridation process.

The relative band positions of Ta$_3$N$_5$ and BaTaO$_2$N were analysed by combining their Mott–Schottky (M–S) plots and UV-Vis results. In Fig. 4a, the flat band potentials of BaTaO$_2$N and Ta$_3$N$_5$ were evaluated according to M–S measurement results to be ca. −0.41 V and −0.32 V vs. NHE, respectively. In consideration of the fact that the bottom of the conduction band (CB) for one n-type semiconductor is normally more negative by ca. 0.2 V than the flat band potential,$^{24,47,46}$ the CB positions of the n-type Ta$_3$N$_5$ and BaTaO$_2$N are estimated to be −0.52 eV and −0.61 eV, respectively. By combining their bandgaps achieved from the UV-Vis results (Fig. 1B), the relative band positions of BaTaO$_2$N and Ta$_3$N$_5$ are then deduced and given in Fig. 4b. Accordingly, the nanocomposite exists as a type II heterostructure, where the excited electrons are expected to transfer from the conduction band of BaTaO$_2$N to that of Ta$_3$N$_5$, while the photogenerated holes will transfer in an opposite way, leading to the spatial charge separation.

The photocatalytic H$_2$ evolution rates on the pristine and modified Ta$_3$N$_5$ samples were examined using the deposited platinum nanoparticle as the reduction cocatalyst in the presence of CH$_3$OH under visible light irradiation (λ > 420 nm). No reaction takes place in the dark, and H$_2$ is evolved only under light irradiation. As given in the half reaction part of Table 1, the rate of H$_2$ evolution undergoes an initial increase and subsequent decrease with the increasing molar ratio of Ba/Ta, and the optimal value of the Ba/Ta molar ratio

![Figure 2](image_url)
Table 1  Photocatalytic performances of typical photocatalysts under visible light irradiation (λ > 420 nm)

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<th>Entry</th>
<th>H2-evolving photocatalysts</th>
<th>Surface area (m² g⁻¹)</th>
<th>H2 evolution rate (µmol h⁻¹)</th>
<th>Overall water splitting</th>
<th>Gas evolution rates (µmol h⁻¹)</th>
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<td>16.5</td>
<td>0.6</td>
<td>0.3</td>
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*a* Reaction conditions: 0.15 g of 0.5 wt% Pt/Ba(n)-Ta3N5 (n = 0–1) and 0.5 wt% Pt/Ta3N5/BaTa2O3N (0.3)-mix samples; 0.15 g of La2O3; aqueous methanol solution (150 mL, 20 vol%); 300 W xenon lamp (λ > 420 nm); 1 h irradiation. b Reaction conditions: 30 mg of 0.5 wt% Pt-modified H2-evolving photocatalysts; 50 mg of 0.45 wt% PtOx/WO3 as O2-evolving photocatalyst; 100 mL of aqueous NaI solution (1.0 mM); Pyrex top-irradiation type; 300 W xenon lamp (λ > 420 nm); 1 h irradiation.

Fig. 3  Representative TEM (left) and locally enlarged HRTEM (right) images of the chosen Ba(0.3)-Ta3N5 sample.

Fig. 4  Band structure characterizations of the Ta3N5 and BaTa2O3N samples. (a) Mott–Schottky plot for the Ta3N5 and BaTa2O3N electrodes. Electrolyte: 0.5 M Na2SO4 solution (pH = 8.5, adjusted using NaOH). Frequency: 1000 Hz. (b) The relative band positions of the Ta3N5/BaTa2O3N heterostructure.

is 0.3. Compared to the Ta3N5 (entry 1), BaTa2O3N (entry 9) or Ta3N5/BaTa2O3N (0.3)-mix (entry 10) sample, the H2 evolution rate on the Pt/Ba(0.3)-Ta3N5 photocatalyst is remarkably promoted. The typical time curve of H2 evolution on the Pt/Ba(0.3)-Ta3N5 sample is given in Fig. S3,† in which it is almost linearly increased in the experimental region, demonstrating its good photochemical stability. In addition, only a small amount of N2 (less than 1 µmol) was detected in the initial stage of irradiation. The dependence of the H2 evolution rate on the Pt/Ba(0.3)-Ta3N5 photocatalyst as a function of irradiation wavelength is well consistent with that of the UV-vis spectra (Fig. S4†), indicating that the H2 evolution process is driven by the incident light.

Encouraged by the significantly enhanced H2 evolution rate, we tried to use the pristine or barium-modified Ta3N5 samples as H2-evolving photocatalysts to construct a Z-scheme overall water splitting system together with a PtOx/WO3 and IO3⁻/I⁻ pair as an O2-evolving photocatalyst and redox mediator, respectively. As shown in the overall water splitting part of Table 1, when using pristine Ta3N5 as the H2-evolving photocatalyst (entry 1), no obvious H2 evolution is detected, demonstrating the infeasibility of Ta3N5 itself to drive the Z-scheme overall water splitting performance. However, using the barium-modified Ta3N5 samples as H2-evolving photocatalysts (entries 2–8), overall water splitting with H2/O2 molar ratios of close to 2 : 1 is achieved, and the photocatalytic activity is dependent on the Ba/Ta molar ratio with an optimal value of ca. 0.3. The Z-scheme activities using the barium-modified samples as H2-evolving photocatalysts (entries 2–8) are all higher than those using BaTa2O3N (entry 9) or the mixed sample (entry 10). The AQE was measured using the Ba(0.3)-Ta3N5 sample as the H2-evolving photocatalyst to be 0.1% at 420 nm. The activity trend is similar to the result of the photocatalytic proton reduction reaction, indicating that the overall water splitting performance is rate-determined by the H2-evolving side. In addition, the multiple cycles of time course curves further demonstrate its photochemical stability in the experimental region (Fig. 5). No obvious Ba2+ ion residue is observed in the centrifuged solution after reaction.
Photocatalytic overall water splitting commonly confronts huge challenges from both thermodynamic and kinetic aspects. In the past few decades, many candidate materials have satisfied the thermodynamics requirement, but overall water splitting on them is unfeasible because of the constraint of insufficient reaction kinetics in the H₂ and/or O₂-evolving side. Accordingly, developing strategies to address the water splitting reaction kinetics, which is greatly affected by the charge separation and surface catalytic process, is highly valuable. In this work, we adopt a simple one-pot nitridation approach with an ammonia flow at high temperature to address the key issue of the charge separation and surface catalytic process, respectively. Reaction conditions: 50 mg of Pt/Ba(0.3)–Ta₃N₅, and 50 mg of PtOₓ/WO₃; 100 mL of NaI aqueous solution (1.0 mM); 300 W xenon lamp (λ > 420 nm), top-irradiation.

Conclusions

In summary, a simple one-pot nitridation strategy is adopted for the barium modification of Ta₃N₅ photocatalyst to address its poor photogenerated carrier separation ability as well as H₂-evolving activity. The one-pot nitridation route overcomes well the challenge of low thermal stability in air for (oxy)nitride-related photocatalysts. Based on this, barium ions are partially doped into Ta₃N₅ to inhibit the formation of defects, and the residue amount of barium ions will cause the in situ formation of BaTaO₂N on the surface of Ta₃N₅ to create an intimate interface for the Ta₃N₅/BaTaO₂N heterostructure. Both of the structures favour the enhancement of charge separation efficiency as well as the promotion of the H₂-evolving rate. Finally, we successfully achieve a Z-scheme overall water splitting process under visible light irradiation using the Ba-modified Ta₃N₅ as a H₂-evolving photocatalyst. The fabrication of the heterostructure via a one-pot route is expected to be extended into more (oxy)nitride systems for promoted solar energy conversion.

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