Template-free synthesis of Ta$_3$N$_5$ hollow nanospheres as a visible-light-driven photocatalyst

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1. Introduction

Environmental problems associated with harmful pollutants discharged into our water systems are, in part, generated from rapid-growing technologies and industries, posing severe threats to human health [1, 2]. Although many water purification technologies currently exist (i.e., powder activated carbon, chlorination, polymer membranes, etc.), they each have drawbacks including the inability to remove all classes of organics or potential hazardous by-products [3, 4]. Conversely, photocatalysis provides an energy-efficient and green pathway to completely degrade organic pollutants in water using light activation [5-8]. However, many current photocatalysts, such as TiO$_2$, which are stable against photocorrosion have large bandgaps, and thus, can only utilize photons efficiently in the ultraviolet region, which occupies no more than 4% of the entire solar spectrum [9]. Therefore, finding effective visible-light driven photocatalysts should enable a more significant fraction of the solar spectrum to be captured and lead to increased photodegradative efficiencies [10].

To date, several visible-light-driven photocatalysts, such as In$_{1-x}$Ni$_x$TaO$_4$ [11], Sm$_2$Ti$_2$O$_7$ [12], Ag$_3$PO$_4$ [13], and solid-solution fabrication as in (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) [14], Cu$_2$ZnSnS$_4$ [15] and ZnS-CuInS$_2$-AgInS$_2$ [16], have been investigated. Among these semiconductor photocatalysts, Ta$_3$N$_5$, which has a narrow bandgap of 2.1 eV, utilizes a large fraction of visible light up to 600 nm, has shown significant interest [17].

In addition to their intrinsic properties, the structural features of photocatalytic particles play an important role in improving the performance by increasing the surface area of the material and impeding the recombination of photoexcited hole-electron pairs [18]. In order to enhance the photocatalytic activity, efforts have been made to control the synthesis of Ta$_3$N$_5$ nanoparticles with well-defined sizes and structures. These include Ta$_3$N$_5$ nanotube arrays [19], nanorods [20], nonwoven cloth [21], and microspheres [22]. Among these, hollow nanoparticles have attracted increasing interest among researchers due to their low density, large surface area and wide range of potential applications [23]. A few studies have successfully synthesized Ta$_3$N$_5$ hollow spheres, which showed very promising photocatalytic performance [9, 24]. For example, Wu et al. synthesized...
monodispersed Ta$_3$N$_5$ hollow spheres using poly(styrene-co-acrylamide) (PSAM) colloidal spheres as hard templates. However, the preparation processes for these methods can require significant amounts of energy and time due to the complex synthetic procedures as well as high-temperature calcinations to remove the core templates, which may reduce surface area and thus efficiency.

In this study, we describe a facile process to synthesize tantalum nitride hollow nanospheres (HNS) that does not require hard templates. Here, tantalum oxide HNS are formed via an orchestrated solution-based synthesis and subsequently converted to tantalum nitride HNS via controlled ammonolysis. Evolution of structure, composition and phase is evaluated. In addition, the as-synthesized Ta$_3$N$_5$ nanostructures are utilized to photocatalytically degrade Methylene Blue (MB) dyes in aqueous solution under visible light illumination. The photocatalytic efficiency is evaluated as a function of nitrogen content, which is controlled via annealing. Thus, the fabrication process is not only simple and viable for mass production of Ta$_3$N$_5$ HNS, but also the as-prepared products show significantly enhanced photocatalytic performance for MB dye degradation under visible light over other Ta$_3$N$_5$ nanostructures.

2. Experimental section

2.1. Material preparation
The reagents were of analytical grade and used without purification. Tantalum (V) ethoxide [Ta(OCH$_2$CH$_3$)$_5$], 99.98% was purchased from Sigma Aldrich. Ethanol [C$_2$H$_5$OH] was purchased from Wako. Ammonia gas was supplied by Airgas, Inc. Milli-Q water was used in all experiments.

2.2. Synthesis of tantalum oxide hollow nanospheres
Tantalum oxide hollow nanospheres were prepared via a hydrothermal method. In a typical synthesis process, 130 μl (0.05 M) of tantalum (V) ethoxide was well-mixed with 4 ml of pure ethanol in a scintillation vial with sonication for 5 min. The sol was then added into 10 ml of Milli-Q water in a beaker and a white slurry suspension formed immediately. After vigorous magnetic stirring at room temperature for 5 min, the suspension was transferred into a Teflon-lined cylindrical steel autoclave [23 ml, Parr Instruments, Inc.]. The reactor was sealed and heated at 200 °C for 12 h hours in a convection oven and subsequently cooled to room temperature. The resulting white precipitates were centrifuged, washed three times with deionized water and ultimately dried in a vacuum oven at 60 °C for 12 h.

For the synthesis of Ta$_2$O$_5$ nanorods, the as-prepared Ta(OEt)$_5$/EtOH sol was added into 10 ml of ammonia hydroxide solution to a final pH of 9. The solutions were hydrothermally treated as described above at 200 °C, but for 48 h.

2.3. Synthesis of Ta$_3$N$_5$ hollow nanospheres
Tantalum nitride hollow nanospheres were prepared via thermal ammonolysis. Briefly, the previously-synthesized tantalum oxide HNS powders were heated to 650 °C at 5 °C min$^{-1}$ and held for 4, 8 and 12 h under a constant flow of anhydrous ammonia gas (150 ml min$^{-1}$) followed by cooling to room temperature naturally under a maintained ammonia gas flow. Ta$_3$N$_5$ nanorods and commercial bulk Ta$_3$N$_5$ (C-Ta$_3$N$_5$) were prepared with the same experimental procedures but with a higher nitridation temperature (i.e., 800 °C) for 12 h.

2.4. Characterization
Crystal structure (phase and size) analyses of obtained products were determined by powder X-ray diffraction (XRD, PANalytical Empyrean Series 2) using Cu Kα (λ = 0.1546 nm). Particle sizes and morphologies were characterized using scanning electron microscopy (SEM) on a MIRA3 GMU SEM (Tescan). Validation of particle size, morphology, crystallinity, as well as grain evolution was conducted via bright field imaging and selected area electron diffraction (SAED) using transmission electron microscopy (TEM, FEI Tecnai T-12) at 120 kV. The adsorption band-edges of tantalum oxide and nitrides were determined via optical diffuse reflectance spectra acquired from a UV-VIS-NIR scanning spectrophotometer (Varian Cary 500) with an integrating sphere accessory. The X-ray photoelectron spectroscopy (XPS) characterization was carried out by using a Kratos AXIS ULTRA DLD, XPS system equipped with an Al Kα monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. All XPS spectra were calibrated with C 1s at 284.8 eV. The nitrogen adsorption-desorption measurements were conducted on a Micromeritics ASAP 2020 Plus Physisorption apparatus. The as-synthesized samples were degassed at 250 °C, for 5 h before the measurement. The BET surface area of the samples was measured by multipoint BET method using the adsorption data in a relative pressure (P/P$_0$) range of 0.05–0.3. A desorption isotherm was used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method.
2.5. Photocatalytic tests

Photocatalytic activity of the products was studied by degradation of Methylene Blue (MB) dye in an aqueous solution under visible light irradiation using a 300W xenon lamp (Newport, QE-PV-S1) light source. In a typical procedure, 10 mg of the photocatalyst was added into 50 ml of an aqueous solution of MB (30 μM), which was ultrasonicated for 5 min. The resulting uniform suspension (at pH = 7.5) was magnetically stirred (500 rpm) in air at room temperature (25 °C) in the dark for 1 h to reach the adsorption-desorption equilibrium at the surface of the catalyst before illumination. The photocatalytic activity was investigated by measuring the extent of MB dye concentration, determined by monitoring the intensity of the primary MB adsorption peak (at 664 nm) using an Agilent Cary 60 UV-VIS spectrophotometer. To do this, 3 ml aliquots were collected at different intervals of time (every 10 min) and then centrifuged to remove the solid particles.

3. Results and discussion

The morphology of Ta2O5 hollow nanospheres obtained after hydrothermal treatment at 200°C for 12 h was investigated by SEM and TEM (figures 1(a) and (b)). These mesoporous tantalum oxide HNS have an average diameter of ~113 nm (+/- 22.7 nm) and were used as precursor particles for making tantalum nitride HNS. Selected area electron diffraction (figure 1(c)) of these hydrothermally synthesized particles reveals diffuse rings, suggesting an amorphous or weakly nanocrystalline material. High-resolution TEM (figure S1 is available online at stacks.iop.org/JPCO/3/075010/mmedia) analyses confirms a disordered structure without discernible lattice fringes. Interestingly, bowl-like hollow shells can be formed without hydrothermal treatment (figure S2(a)). These are actually collapsed hollow nanospheres. In fact, in order to obtain these hollow tantalum oxide nanospheres without solid templates, it is essential to control the reaction sequence. The Ta(OEt)5/EtOH mixture sol needs to be added into excessive amounts of water; otherwise, only amorphous aggregates were formed (figure S2(b)). This result is likely explained by an oil (i.e., mixed Ta(OEt)5/EtOH) in water emulsion formation mechanism, which could provide an interface for the formation of the ultrathin tantalum oxide shells [25]. Indeed, when a highly reactive metal (e.g., pentavalent) with relatively short chain alkoxy groups reacts with water, the hydrolysis kinetics are fast and condensation can commence [26, 27]. In this case (metal alkoxy in solvent added into water), solid material is deposited within this interfacial region between the oil and water phase, yielding a hollow shell. Conversely, if water is added into a solution of the precursor, hydrolysis occurs before micelle formation, and thus no HNS can be formed. It is also worth noting that HNS with larger sizes up to 800 nm can be produced by simply decreasing the ethanol to water solvent ratio to 1:20 (figure S2(c)).
likely that low ethanol content would favour the micelle formation as the immiscibility between the alkoxide and water can be decreased by ethanol addition \[28\]. When these reactions are carried out at room temperature (i.e., not under hydrothermal conditions), the extent of mass transport of metal oxide/hydroxide species and condensation reactions are reduced, leading to a decrease in integrated networks of metal oxides, likely leading to reduced stiffness and subsequent collapse of these HNS. Utilizing hydrothermal conditions enables additional hydrolysis/polycondensation reactions to occur between precursors, forming stiffer metal oxide frameworks \[29\] and leading to well-defined hollow nanospheres with stabilized structures. In addition, the high temperature and pressure of these reactions can induce Ostwald ripening that not only connects loosely aggregated amorphous particles to each other \[30\], but also leads to the formation of pores within the shell. As additional ripening occurs, the walls of HNS become thinner and a mesoporous tantalum oxide HNS is formed.

Representative SEM and TEM micrographs of Ta$_3$N$_5$ hollow nanospheres (figures 1(d) and (e)) prepared from the direct nitridation of Ta$_2$O$_5$ HNS at 650 °C for 12 h under ammonia flow demonstrate that the morphology of the initially synthesized spherical particles is retained without an obvious change in the particle size (figure S3). A selected area electron diffraction pattern (figure 1(f)) obtained from the area depicted in figure 1(e) presents multiple strong diffraction rings at d-spacings of 0.160 nm, 0.229 nm, 0.248 nm, 0.256 nm, 0.284 nm, 0.362 nm, and 0.511 nm, which correspond to the (−3 1 5), (−4 0 2), (1 1 3), (3 1 0), (−2 0 3), (1 1 0), and (2 0 0) crystal facets of monoclinic Ta$_3$N$_5$, respectively. This confirms that phase pure Ta$_3$N$_5$ can be obtained at significantly reduced nitridation temperatures (i.e., more than 150°C lower) than former studies commonly required to complete the nitridation of Ta$_2$O$_5$ nanoparticles \[20, 31, 32\]. This reduced nitridation temperature is likely attributed to enhanced diffusion of reactive nitriding species within the hollow thin shell structure as well as the ability to transform highly disordered (i.e., amorphous) particles with small sizes \[19, 24, 33\].

X-ray diffraction (XRD) of powdered samples (figure 2(a)) was performed in order to further confirm the phase change of the tantalum oxide starting materials under various nitridation times at 650°C. Consistent with previous results, tantalum oxide HNS initially consisted of amorphous/weakly nanocrystalline domains, subsequently undergoing a phase transition to a crystalline nitried material after annealing for at least 4 h under ammonia flow. All diffraction peaks for these samples (i.e., nitried longer than 4 h) are characteristic of...
monoclinic Ta$_3$N$_5$ (JCPDS Card No. 89–5200). Photographs of the as-annealed Ta$_3$N$_5$ HNS products (figure 2(b)) demonstrate a significant color change with elongated nitridation times, from white to brown and then eventually a bright red. This result matches well with the optical properties of the hollow nanospherical materials, which were characterized by measuring the UV-Vis diffuse reflectance spectra, as shown in figure 2(c). The adsorption band-edge for tantalum oxide and Ta$_3$N$_5$(12 h) HNS are at 310 nm and 600 nm, corresponding to the reported bandgap values of 4.0 eV and 2.1 eV, respectively. The conduction and valence bands of Ta$_3$N$_5$ are contributed to the Ta 5d and N 2p orbitals, respectively. The large red shift after nitridation is hence caused by the substitution of nitrogen atoms, whose 2p orbitals have higher potential energy than oxygen atoms, narrowing the bandgap greatly by shifting the valence band upward [34, 35], also enabling the visible-light-driven ability. Moreover, the band structure of Ta$_3$N$_5$ HNS (8 h) is calculated to be at approximately 2.2 eV, slightly higher than that of the sample annealed for 12h, which is in good agreement with the subtle color difference between these two products. Both 8 h and 12 h samples show a similar crystallinity (as observed in the full width at half maximum (FWHM) of peaks in the XRD patterns, figure 2(a)). Conversely, HNS heated at 650 °C for 4h shows a relatively larger bandgap (2.4 eV), indicating an incomplete conversion to the nitride.

X-ray photoelectron spectroscopy (XPS) was also carried out to further investigate the composition of the Ta$_3$N$_5$ HNS annealed at 650°C for different durations (i.e., 4 h, 8 h, and 12 h). Only Ta, C, O and N elements were found in the survey spectrum (figure S4). Deconvoluted Ta 4f spectra (figure 2(d)) of the nitrided samples revealed four peaks. The binding energies for the Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ peaks at 25.3 and 27.1 eV represent Ta$^{5+}$ of Ta$_3$N$_5$ [36]. In addition, the Ta 4f$_{7/2}$(Ta$_2$O$_5$) [26.5 eV] and Ta 4f$_{5/2}$(Ta$_2$O$_5$) [28.4 eV] peak intensities decrease with longer nitridation times, indicating that oxygen content is reduced, but still remains in the system even after 12 h of nitridation at 650 °C. This is further confirmed by the XPS analysis of the tantalum oxide HNS sample (figure S5). XPS analysis of N 1s spectra revealed N$^-$ in Ta$_3$N$_5$ with a typical value of 396.8 eV. Notably, a small peak with higher binding energy exists in the 4h specimen and decreases with a longer nitridation duration, which could be ascribed to the N-Ta-O species [37]. This is likely as nitrogen has a lower electronegativity (3.04) than oxygen (3.44) and hence there is a nearest-neighbor effect to increase the binding energy [38]. The O 1s spectra of Ta$_3$N$_5$ HNS samples show a main peak centered at 530.2 eV, which was associated with O-Ta bonding. The other O 1s peaks present at ~532 eV could be related to residual organic ligands (e.g., alkoxy groups), −OH groups, or even carbonate contamination on the surface of the products [39, 40].

To further investigate crystalline grain growth, structural integrity and pore evolution of the hollow nanospheres during nitridation, high resolution TEM (HRTEM) analyses was performed. Direct observations based on the TEM micrographs indicated that Ta$_3$N$_5$ HNS annealed at 650 °C for 4 h exhibited the smallest crystal domains (figure 3(a)) with grain sizes significantly increasing with longer nitridation times (figures 3(b), (c)). This was corroborated with crystallite size calculations (Table S1) using the Scherrer equation. It is also important to point out that the grain size increases only slightly when the annealing time was increased from 8 h to 12 h, indicating the grain growth kinetics were significantly impeded by boundary interactions amongst different grains [41]. Closer observation of these HNS using HRTEM revealed the evolution of grain growth of the Ta$_3$N$_5$ spheres with increased reaction times. Weakly crystalline grains within an amorphous matrix were observed in the 4h sample (figure 3(d)), while highly crystalline grains that are interconnected were observed in Ta$_3$N$_5$ HNS annealed at 8 h and 12 h (figures 3(e), (f)). In addition, a larger fraction of sintered particles, larger pores and more porosity were introduced to the hollow spherical particles with increased nitridation time. This can also be explained that during crystallization, mass transport can occur between smaller, high surface area particles or with larger particles to reduce overall free energy [30, 42]. This mass transfer also causes increasing strain within the HNS shell, together with the volume shrinkage resulting from the nitrogen and oxygen atom substitution, which increases the porosity and yields a mesoporous material [43].

In order to investigate this change in porosity, nitrogen adsorption/desorption isotherms of as-synthesized Ta$_3$O$_5$ HNS and Ta$_3$N$_5$ HNS nitrided for 12 h were investigated (figure 3(d)). The Brunauer-Emmett-Teller (BET) surface area was reduced from 140.84 m$^2$ g$^{-1}$ for tantalum oxide HNS precursor particles to 73.41 m$^2$ g$^{-1}$ for Ta$_3$N$_5$ HNS (12 h) likely due to grain growth during the nitridation treatment. Furthermore, the corresponding Barrett-Joyner-Halenda (BJH) analysis reveals the existence of ~7.5 nm pores in the oxide HNS, while those in nitrided HNS increased to a diameter of 18.67 nm. The table from figure 3(e) shows the summary BET surface area and pore size results for all other Ta$_3$N$_5$ photocatalyst specimens. Here, it is likely that the surface area of the Ta$_3$N$_5$ HNS significantly decreased with nitridation times due to an increase in grain size, whereas the pore size increased, corroborating our HRTEM results. The synthetic Ta$_3$N$_5$ nanostructures possess significantly higher surface area (~20 times more) than the tantalum nitride obtained from commercial bulk Ta$_2$O$_5$ with the same nitridation technique, highlighting the advantages of the solution-based precursor particle method utilized here.

The photocatalytic performance of the nanostructures was explored by investigating the degradation of Methylene blue (MB) solutions under visible light irradiation. For the sake of comparison, Ta$_3$N$_5$ nanorods and
bulk Ta$_3$N$_5$ particles (figure S6) made from commercial tantalum oxide were tested in parallel with the as-prepared Ta$_3$N$_5$ HNS synthesized at different nitridation times (i.e., 4 h, 8 h and 12 h). As illustrated in figure 4(a), the negative control ('blank test', no photocatalyst) showed a negligible amount of MB being degraded. After 60 min of exposure to light, almost all of the dye was removed using phase pure Ta$_3$N$_5$ HNS (8 h, and 12 h). UV-vis absorption spectra of MB for Ta$_3$N$_5$ HNS$_{12h}$ sample were included in figure S7. We note that this sample showed a shift in the MB adsorption peak at 663 nm to shorter wavelengths, indicating the N-demethylation upon dye breakdown [44]. However, only 63% and 90% of the initial dye was degraded by C-Ta$_3$N$_5$ and Ta$_3$N$_5$ nanorods, respectively. There is negligible photodegradation of MB when tantalum oxide HNS was examined, indicating that the oxide-based hollow oxide spheres could not be activated using visible-light. The MB degradation data (figure 4(b)) was subsequently analyzed with a pseudo-first-order model [45], 

$$-\ln(C/C_0) = kt$$

where $t$ is time and $k$ is the reaction rate constant. Clearly, the Ta$_3$N$_5$ HNS specimen annealed for 12 h shows the highest reaction rate, which is roughly 2 and 5 times better than that of Ta$_3$N$_5$ nanorods and C-Ta$_3$N$_5$, respectively. Thus, the relative photocatalytic performance of the nitrided photocatalysts follow the order: HNS$_{12h}$ > HNS$_{8h}$ > nanorods > HNS$_{4h}$ > C-Ta$_3$N$_5$. To improve the performance of photocatalysts, it is vital to understand the key factors that control their photocatalytic efficiency. Crystallinity and crystallite size are necessary to be considered as higher crystallinity can reduce the number of defects, while a
smaller crystallite size can decrease the migration distance for excitons to surface reaction sites. Furthermore, a larger surface area to increase the number of active surface sites as well as the surface charge carrier transfer rate, and a suitable band engineering to better utilize the energy from incident light are also generally desired in a photocatalytic system. Based on these photodegradation results, it can be reasonably inferred that the overall hollow nanosphere structure shows superior photocatalytic activity versus bulk Ta3N5 and rod-like Ta3N5. Besides the fact that the HNS have a significantly larger surface area compared to the other solid structures, their hollow nature increases the light utilization efficiency because of the potential for multiple light interactions within their structures [32]. In addition, the formation of a mesoporous structure can further enhance the physicochemical properties while the pores can enable a more efficient transport for small MB molecules to the active sites on the photocatalytic surfaces of the particles [46, 47].

Comparatively, the Ta3N5 HNS sample annealed for 4 h shows a significantly lower photodegradation efficiency than that of HNS with longer nitridation times. This specimen, which has a much larger surface area and smaller crystallite size, is likely less active than the 8 and 12 h samples due to two main reasons. Besides the slightly larger bandgap, there is a large amount of residual oxygen impurities retained in the lattice. The presence of these oxygen ‘defects’ might be the major reason contributing to the suppressed photocatalytic activity because they can operate as trapping and recombination centers between photogenerated charge carriers [48]. In addition, there are residual amorphous regions around the crystalline domain boundaries of the Ta3N5 nanocrystals which might increase the resistance for transport of the photogenerated electron and hole pairs [49]. It is also worth noting that despite the similar grain size, crystallinity, bandgap and even a larger surface area, the Ta3N5 HNS_8 h contains more oxygen (figure 2(d)) and exhibits a slightly inferior photodegradation performance over Ta3N5 HNS_12 h. This evidence indeed suggests the role of oxygen as an impurity which reduces photocatalytic efficiency.

4. Conclusion

We synthesized Ta3N5 hollow nanospheres as photocatalysts for water purification via a template-free solution route to form tantalum oxide HNS, which were subsequently thermally nitrided. The potential formation mechanism and structural evolution of the hollow nanospheres are discussed. The as-obtained Ta3N5 HNS presents a superior photocatalytic performance for methylene blue dye (and potentially other organic pollutants) degradation under visible light irradiation compared with other Ta3N5 nanostructures. The high photocatalytic efficiency is attributed to the unique mesoporous structure, high specific surface area, high crystallinity with few oxygen defects and a potential for multiple light interactions within the hollow spheres. Clearly, the presence of amorphous regions and residual oxygen content in the nitrided product are key limiting factors in the photocatalytic performance of these HNS. However, increasing the annealing temperature or extending thermal treatment duration will lead to the collapse of the HNS structures. Future efforts are now underway to optimizing nitridation procedures while maintaining the HNS structure.
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