Narrow-bandgap Nb₂O₅ nanowires with enclosed pores as high-performance photocatalyst

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ABSTRACT Porous niobium oxide nanowires synthesized via a solvothermal method exhibited decreased bandgap, enhanced light absorption and reduced charge-recombination rate. The porous Nb₂O₅ nanowires showed increased performance for the photocatalytic H₂ evolution and photo-degradation of rhodamine B, as compared to their solid counterparts, which could be ascribed to the peculiar porous nanostructure.

Keywords: niobium oxide, nanowires, photocatalysis

INTRODUCTION

Niobium(V) oxide (Nb₂O₅) is an important n-type transition metal oxide semiconductor with a bandgap of 3.4 eV, similar to TiO₂ (3.2 eV), which has been demonstrated as a promising material in gas sensing, electrochromics, acid catalysis, field emission displays, batteries, solar cells and other electronic devices [1–7]. In particular, nanostructured Nb₂O₅ offers high surface to volume ratios and quantum confinement effects that enable unique physical and chemical interactions at the surface [8–10]. As a result, such morphological manipulations significantly influence the optical and electronic properties of Nb₂O₅. However, there are few studies of Nb₂O₅ for photocatalytic applications due to two intrinsic drawbacks: the large bandgap (ca. 3.4 eV), which limits its application in the visible region and the fast recombination rate of photogenerated electron-hole pairs (e[−]/h⁺), which reduces the quantum efficiency of the photo-induced redox reaction. A recent study of reduced Nb₂O₅ nanorods attributed enhanced light absorption, improved charge separation and transport capability and photocatalytic performance to the presence of substantial Nb⁴⁺

cations and oxygen vacancies [11].

One dimensional (1D) nanostructured photocatalysts provide a continuous long carrier transfer path and can be separated and recycled easily because of their large aspect ratio [12–14]. Among the many varieties of 1D nanostructures, porous nanowires are particularly interesting, not only for the unique porous structure and physical chemical properties, but also for their outstanding performance in optics and electronics [15–23]. So far, many groups have reported the growth of porous 1D semiconductor nanostructures and studied their exceptional performance, such as porous ZnO nanowires with superior photocatalytic activity [24], CdS nanosponges showing high activity for RhB photo-degradation under visible light due to the accessibility of both inner and outer surfaces through the pores in the walls [25], porous TiO₂ nanotubes with improved photocatalytic efficiency due to their larger specific surface areas [26], porous In₂O₃ nanowires with excellent gas sensing properties to H₂S benefiting from surface adsorption and the sulfuration [27], porous SnO₂ nanowire bundles consisting of interconnected nano-crystallites with a remarkable photocatalytic effect for the degradation of RhB and a high de-lithiation capacity [15], and porous Co₃O₄ nanowires with high sensitivity to carbon monoxide because porous structure increases the surface reactive sites and facilitates the diffusion of target gases [28]. These advantages come from the effective diffusion and adsorption of reactant in the porous nanostructures. Porous nanostructures can also induce a change in electronic structures of materials. For instance, Wan *et al.* [29] synthesized porous Ag₃PO₄ nanotubes which exhibit higher photocatalytic activity than irregular Ag₃PO₄

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powder for the reduced band gap of 2.47 eV and enhanced UV-vis absorbance.

Different from all these reports of porous nanostructures, we report herein our recent discovery on pseudo-hexagonal tef-tef (TT) Nb₂O₅ nanowires with an enclosed porous structure which show enhanced photocatalytic activity over their nonporous nanowire counterparts for the decomposition of Rhodamine B (RhB) in aqueous solution. We also reveal that a red shift of the absorption edge between nonporous Nb₂O₅ nanowires (npNW) and porous nanowires (pNWs) annealed at appropriate temperature leads to the bandgap decrease from 3.22 to 2.95 eV, changes the pathway of RhB degradation and significantly enhances the photocatalytic H₂ evolution from the water.

EXPERIMENTAL SECTION

Solvothermal synthesis of porous Nb₂O₅ nanowires (pNW-580)

In a typical synthesis, ammonium niobate(V) oxalate hydrate (9.57 mmol) and oleic acid (OA) (2 mL, 90%, Aldrich) were mixed with trioctylamine (TOA) (13 mL, 98%, Aldrich) in a three-necked round bottom flask with vigorous stirring for 12 h and sonication for 20 min. The mixture was transferred into a 45-mL Teflon-lined autoclave and then heated at 453 K for 6 h. The white precipitates were filtered off, washed several times with ethanol and water, and dried at 353 K for several hours. The dried precipitate was then calcinated at 580°C for 1 h, and collected. The samples calcinated at 400, 600 and 700°C were also collected for comparison and denoted similarly. For instance, pNW-600 stands for the sample annealed at 600°C.

Hydrothermal synthesis of npNW

The npNWs were synthesized through a simple hydrothermal method using Nb metal powder and urea as starting materials. In a typical synthesis, Niobium powder (0.122 g) was put into a 65 mL urea solution (1–2 mol L⁻¹), and then the mixture was transferred into a 100-mL Teflon-lined autoclave and heated at 453 K for 4–7 days. Then the white precipitate was collected by centrifugation and washed several times with ethanol and water. npNWs were obtained by calcination of the dried precipitate at 500°C for 2 h.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X-ray diffractometer by using Cu Ka

radiation ($\lambda=0.154$ nm, 40 kV/40 mA). Transmission electron microscopy (TEM) images were collected on a JEM-2100 operated at an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) images were taken using a Hitachi S-4800 scanning electron microscope. Diffuse reflection spectra were recorded on a UV-vis-NIR spectrometer (Analytik jena; SPECORD plus210) and were converted from reflection to absorbance by the Kubelka-Munk method. The photoluminescence (PL) spectra of the as-synthesized samples in the powder form were investigated at room temperature on a Fluoromax-4 fluorescence spectrophotometer (Horiba Jobin Yvon Japan) with an excitation wavelength (λ_{ex}) of 325 nm and the width of the excitation and emission slit were 5 and 2 nm, respectively. The emission spectrum was monitored over a wavelength range of 360–600 nm.

Photocatalytic tests

The photocatalytic activity of the samples (pNWs and npNWs) for hydrogen evolution was evaluated in a closed gas circulation and evacuation system under visible light illumination ($\lambda>420$ nm). Typically, 0.020 g of powder sample was dispersed in 60 mL aqueous solution containing 0.25 mol L⁻¹ Na₂S and 0.35 mol L⁻¹ Na₂SO₃ in a Pyrex reaction cell. The light source was a 500-W Xe lamp supplying the full wavelength illumination. The amount of produced hydrogen was analyzed with on-line gas chromatograph (GC7900, thermal conductivity detector, high-purity nitrogen as carrier gas).

The photocatalytic activity of the samples (pNWs and npNWs) in degradation of RhB was evaluated in aqueous solution. Typically, 50 mg of photocatalyst was added into 50 mL aqueous solution of RhB (5 mg L⁻¹) in a reactor with sonication. The solution was continuously stirred for 1 h in the dark to ensure the establishment of adsorption-desorption equilibrium between the photocatalyst and RhB before irradiation. Then the solution was illuminated by a 250-W high-pressure mercury lamp with wavelength centred at 365 nm. During the degradation, the RhB solution containing photocatalyst was continuously stirred by a dynamoelectric stirrer and the concentration of RhB was monitored with a SPECORD 210 PLUS UV-vis spectrometer (Jena).

RESULTS AND DISCUSSION

Powder XRD was used to characterize the structure of the as-prepared samples, as shown in Fig. 1a. The reflection peaks of porous nanowires pNW-580 and nonporous nanowires npNW can be well indexed to the pseudo-

Figure 1 (a) XRD pattern of the porous nanowires pNW-580 and nonporous nanowires npNW; TEM images of (b) the porous nanowires pNW-580 and (c) nonporous nanowires npNW. HRTEM images of the (d) porous nanowires pNW-580 and (f) nonporous nanowires npNW with (e) and (g) as constructed inverse FFT images from the selected areas (d) and (f). Inset of (d) shows the electron diffraction pattern of the pNW-580.

hexagonal TT phase of Nb_2O_5 (JCPDS number 28-0317), with lattice constants of $a=3.607 \text{ \AA}$ and $c=3.925 \text{ \AA}$. Interestingly, the porous nanowires pNW-580 show a better crystallinity than the nonporous nanowires npNW. The SEM images as shown in Fig. S1 and the TEM images in Fig. 1b and c reveal the morphology and structure of the porous and nonporous nanowires, respectively. While the npNWs are typically longer than $5 \mu\text{m}$ and show ripple-like contrast in TEM due to bending-induced strain, the porous NWs pNW-580 are typically shorter than $1 \mu\text{m}$ and featured with well-separated pores inside the nanowires. The diameter of the pores falls into the range of $5\text{--}10 \text{ nm}$ and the pores do not move towards the surface of nanowires in the TEM image after large-angle rotation of the TEM holder, which indicates that all the pores are fully trapped within the nanowires. High resolution TEM (HRTEM) image of the nanowires in Fig. 1d and the fast Fourier transformation (FFT) pattern in the inset show that all the porous nanowires are single crystalline and oriented along c -axis. The clear lattice fringes perpendicular to growth direction of the nanowires show a spacing of $3.97 \text{ \AA}$, corresponding to the (001) crystal planes of pseudo-hexagonal Nb_2O_5 . The reconstructed crystal lattice based on the FFT pattern obtained from the porous area (Fig. 1e) shows that the lattice surrounding the pores are severely twisted. On the contrary, the npNWs show solid structure and non-twisted lattice fringes separated by $3.97 \text{ \AA}$ with the same growth direction along c -axis, as shown in the HRTEM of Fig. 1f and reconstructed crystal lattice of Fig. 1g. The annealing temperature after sol-

vothermal treatment has a significant impact on the morphology and phase stability of the porous nanowires. As shown in the TEM image of Fig. S2, the porosity of pNW-600 is much higher than pNW-580 while the crystallinity of pNW-600 apparently decreases. In addition, increased annealing temperature causes the gradual formation of orthorhombic phase in pNW-600 and pNW-700 while pNW-580 is pristine TT-phase, as is shown in Fig. S3.

The formation of enclosed-pore structure was generally considered as a result of ligand assembly process. The ligands of OA and TOA replaced the oxalate anion and coordinated with the Nb center as structure directing agent at an elevated temperature. Hydrophobic interactions between methylene chains of the TOA and OA molecules in 3D space lead to self-assembly structure with hydrophobic core and surrounding Nb species. After removing the organic template by calcination at 853 K , the cores transform into pores and the coordination structure forms crystalline porous nanowires of Nb_2O_5 .

Diffuse reflectance UV-vis spectroscopy was employed to study the optical properties of the porous nanowires pNW-580, pNW-600 and the nonporous nanowires (npNWs), as shown in Fig. 2a. The absorption spectrum of the pNW-580 shows a sharp absorption edge at 2.95 eV or 420 nm , deduced by extrapolation of the linear part of the rising absorption curve, which red-shifts from the edge of the npNWs at 3.22 eV or 385 nm (Fig. 2b). The decreased band gap of pNW-580 can be attributed to the mid-gap states formed by the under-coordinated ions

Figure 2 (a) Diffuse reflectance spectra and (b) plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) of the porous pNW-580, pNW-600 and nonporous Nb₂O₅ nanowires with the absorption edge indicated in the legend of (b).

in the twisted lattice surrounding the pores. These results clearly reveal that lower bandgap of pNW-580 could be attributed to the unique enclosed porous structure. However, the pore structure does not lead to mid-gap states and decreased bandgap, as can be found in the case of pNW-600. The absorption edge of pNW-600 falls at 3.14 eV, which is significantly upshifted from pNW-580 and close to npNWs. It is possibly due to the re-configuration of the under-coordinated atoms around the pores through annealing at higher temperature during the phase transition from pseudo TT to orthorhombic Nb₂O₅. The mid-gap states are also removed through this process. Comparison of the Raman spectra of the different nanowires (Fig. S4) indicates the decreasing bond order of the Nb–O polyhedra and disordered structure in pNW-580 can be attributed to the increased oxygen vacancies [30].

Since the band gap of the pNW-580 falls into the visible range, they could be considered as a potential candidate for high-performance photocatalysts. They were first evaluated in the photocatalytic degradation of RhB in aqueous solution under ultraviolet irradiation and compared to the performance of npNWs. As shown in Fig. 3a, the maximum absorption of the RhB solution exhibits significant hypsochromic shifts under ultraviolet irradiation in the presence of pNWs. The shift of maximum wavelength from 556 to 498 nm is completed after irradiation for 50 min, which corresponds to the *N*-deethylation of RhB in the photocatalytic degradation [31]. However, in the presence of npNWs of Nb₂O₅, the characteristic absorption of RhB around 556 nm decreases to about zero within 180 min, in a mineralization process with no wavelength shift for the maximum absorption of the solution during the whole degradation process (Fig. 3b). Similar mineralization degradation of

RhB under UV light irradiation is observed when commercial Nb₂O₅ and pNW-600 are used, but with a much slower reaction rate, as shown in Fig. 3c and Fig. S5.

A pseudo-first-order equation was applied to describe the kinetic data for the as-prepared samples and commercial Nb₂O₅, as is shown in Fig. 3d. The apparent rate constant was calculated to be $k=0.047 \text{ min}^{-1}$ for the porous nanowires, $k=0.011 \text{ min}^{-1}$ for the npNWs and $k=0.0032 \text{ min}^{-1}$ for the commercial sample. The rate constant of the pNWs is 4 times that of the npNWs, and 15 times that of commercial Nb₂O₅, demonstrating excellent photo-degradation capability of the pNWs.

To further investigate the photo-catalytic activity of the porous nanowires, we evaluated their performance of the photo-degradation of RhB under visible light ($\lambda > 420 \text{ nm}$) irradiation. As shown in Fig. S6, the photo-decomposition of the RhB induced by visible-light in the presence of pNW-580 is significant with 90% of RhB decomposed after 60 min irradiation. In addition, similar characteristics of maximum absorption shift are observed between UV-light and visible-light photolysis according to the light absorption measurement.

The *N*-deethylation of the fully *N,N,N',N'*-tetra-ethylated rhodamine species by OH radicals is a surface reaction on the photocatalysts [32,33]. In our case, different UV-vis degradation spectra of RhB (Fig. 3) suggest that the degradation of RhB is dominated by different degradation pathways in the presence of different Nb₂O₅ photocatalysts. The mineralization pathway of RhB indicates that OH radicals are dominating the oxidation reactions, while the *N*-deethylation of RhB indicates the direct oxidation of dye molecules by the valence band holes [33]. The valence band potential of regular Nb₂O₅ materials at 2.7 V (vs. normal hydrogen electrode (NHE)), is more positive than the $\cdot\text{OH}/\text{H}_2\text{O}$ redox po-

Figure 3 The UV-vis spectra of RhB photo-degradation by (a) pNWs, (b) npNWs and (c) commercial Nb₂O₅ under UV irradiation, (d) the photo-degradation rate curve of the samples of pNWs, npNWs and commercial Nb₂O₅.

tential (2.38 V vs. NHE) [2]. So the photo-generated holes on the valence band of regular Nb₂O₅ are able to oxidize water to produce free OH radicals and the free OH radicals will dominate the oxidation of dye and lead to the mineralization of RhB. Compared to regular Nb₂O₅, the pNW has a much narrower bandgap, which shifts from 3.28 to 2.88 eV. As shown in the XPS valence-band spectra of the porous and nonporous nanowires of Nb₂O₅ in Fig. S7, the porous nanowires exhibit a valence-band-maximum 2.87 eV below the Fermi level while the nonporous ones 3.08 eV. Assuming the relatively constant Fermi level, the valence band maximum shifts upward of 0.21 eV. This is in reasonable agreement with the band-gap shrink of 0.3 eV and indicates change of the dye-oxidation pathway. With the shrink of the band gap, the valence band potential of the pNW-580 becomes more negative than the redox potential of the $\cdot\text{OH}/\text{H}_2\text{O}$ redox couple. Thus the holes on the valence band of pNWs are not able to oxidize water to form OH radicals. And the adsorbed dye molecules on the catalyst surface will be oxidized by the holes as the primary reaction pathway, which results in the *N*-deethylation product as the main degradation product.

The photocatalytic performance of the pNWs was further evaluated in hydrogen evolution reaction and

compared with npNWs and P25, as shown in Fig. 4a. It is clear that the hydrogen evolution rate of the pNW-580 ($243.8 \mu\text{mol g}^{-1} \text{h}^{-1}$) is much higher than that of npNW (ca. $113.1 \mu\text{mol g}^{-1} \text{h}^{-1}$) and P25 powder (ca. $129.6 \mu\text{mol g}^{-1} \text{h}^{-1}$), suggesting that the creation of pores in the nanowires significantly improves the photocatalytic activity for H₂ evolution. To further evaluate their catalytic stability, all the photocatalysts were recovered and reused for photocatalytic H₂ production under the same conditions. As shown in Fig. 4b, there is nearly no loss of hydrogen evolution rate for both porous and nonporous nanowire photocatalysts, whereas the catalytic activity of P25 evidently declined after 3 cycles. This confirms that the obtained pNWs are much more stable than the commercial product P25 while maintaining a higher photocatalytic activity.

The photocatalytic properties of oxides strongly depend on the band gap, crystallinity and surface area. Generally, large surface area enhances the physical adsorption of reactants and the dispersibility of the powdered photocatalysts. However, the measured Brunauer-Emmet-Teller (BET) surface area for the porous and nonporous nanowires is 38.2 and 37 m² g⁻¹ respectively and with similar pore-size distribution (Fig. S8). The negligible difference in this value implies that surface structure and

Figure 4 (a) Photocatalytic H₂ production efficiency of pNW-580, npNW and P25. (b) Results of reusability experiments for photocatalytic H₂ generation using the three photocatalysts.

electronic properties, rather than surface area, are the key factors for the observed difference in catalytic performance of porous and nonporous nanowires. The high performance of porous nanowires pNW-580 is significantly attributed to the improved light absorption due to their decreased band gap. As shown in Fig. 2a, the pNWs of pNW-580 show an obvious redshift of 35 nm in the absorption edge, as compared to the nonporous nanowires of npNW. In addition, high crystallinity promotes the efficient transfer of photo-generated carriers from bulk to surface by the suppression of charge recombination process. The crystallinity of the pNW-580 is significantly higher than that of the npNW as shown in the XRD results, in spite of the disturbance of the crystal lattice by the introduction of nanopores. Moreover, the pores inside the nanowires possess a large interfacial region and rich structure defects like the oxygen vacancies and under-coordinated Nb, which can trap the photo-generated electrons, decrease the direct electron-hole recombination and improve the charge carrier separation to a great degree [34–36]. The efficient separation of electrons and holes in the pNW-580 is further confirmed by the PL spectra. As shown in Fig. S9, the pNWs exhibit much lower emission intensity than nonporous nanowires, indicating that the recombination of charge carriers is inhibited in this porous structure. As for the comparison between pNW-580 and pNW-600, the even higher annealing temperature and increased porosity in pNW-600 does not bring about better performance than pNW-580 probably due to the reconfiguration of the surface atoms around the enclosed pores during phase transition which leads to the removal of the defects and the mid-gap states. In addition to the increased bandgap and decreased absorption, the lower crystallinity of pNW-600 and inefficient charge separation further exacerbate

the sluggish reaction of RhB degradation.

CONCLUSIONS

In summary, Nb₂O₅ nanowires with enclosed pores were successfully synthesized *via* hydrothermal process. The porous nanowires synthesized at appropriate temperature display better performance than nonporous nanowires of Nb₂O₅ and commercial photocatalyst, such as fairly high photocatalytic activity in the photocatalytic degradation of RhB and hydrogen evolution under both UV and visible-light irradiation. The unique porous structure of Nb₂O₅ nanowires may play the pivotal role in tuning the performance by narrowing the band gap, enhancing the visible light absorption and increasing charge separation efficiency. We hope the trapped-pore induced photocatalytic enhancement could be further explored and applied to the design of high-performance photocatalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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内嵌孔型窄带隙Nb₂O₅纳米线及其光催化研究

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摘要 本论文介绍了一种通过溶剂热制备内嵌孔型氧化铌纳米线的方法. 该方法得到的氧化铌材料能带显著变窄, 吸光范围大幅增加, 电子空穴复合速率降低. 相比于无孔Nb₂O₅纳米线和商业粉末, 这种多孔纳米线显示出卓越的光催化析氢性能和罗丹明染料降解效果, 这都与其特殊的内嵌孔构造存在着密切关系.