Journal of Nanophotonics

Nanophotonics.SPIEDigitalLibrary.org

Structure and photocatalytic performance of layered HNbWO_6 nanosheet aggregation

Li-Fang Hu
Rui Li
Jie He
Liang-guo Da
Wei Lv
Jin-song Hu

SPIE.

Structure and photocatalytic performance of layered HNbWO_6 nanosheet aggregation

Li-Fang Hu,^{a,b} Rui Li,^b Jie He,^{b,*} Liang-guo Da,^a Wei Lv,^b and Jin-song Hu^b

^aAnhui University of Science and Technology, School of Earth and Environment, 168 Shungeng Road, Huainan 232001, China

^bAnhui University of Science and Technology, School of Chemical Engineering, 168 Shungeng Road, Huainan 232001, China

Abstract. Layered HNbWO_6 nanosheet aggregation (e- HNbWO_6) has been assembled by HNbWO_6 nanosheet via an exfoliation-restaking route. The as-prepared samples are characterized by means of powder x-ray diffraction, scanning electron microscope, high-resolution transmission electron microscopy, laser Raman spectroscopy, ultraviolet-vis diffuse reflectance spectroscopy, and N_2 adsorption-desorption isotherms. The photocatalytic performances of the as-prepared samples are evaluated by degradation of methylene blue (MB). The results revealed that e- HNbWO_6 has a specific surface area of about $156.5 \text{ m}^2 \text{ g}^{-1}$, and exhibits a relatively excellent photocatalytic performance for degradation of MB under UV light. © 2015 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JNP.9.093041](https://doi.org/10.1117/1.JNP.9.093041)]

Keywords: HNbWO_6 ; e- HNbWO_6 ; microstructural feature; photocatalytic performance.

Paper 15089 received Aug. 24, 2015; accepted for publication Oct. 27, 2015; published online Dec. 10, 2015.

1 Introduction

As early as about 80 years ago, Hauser and Reed^{1,2} reported that bentonite clay minerals could easily disperse well in water and yield a colloidal suspension as a consequence of spontaneous exfoliation or delamination. The emergence of bentonite suspension marked the beginning of the nanoflake materials era. The term “nanosheet” was defined and used until 1996 by Sasaki et al.³ to reflect the peculiar features of both molecular thickness and extremely high two-dimensional (2-D) anisotropy. Graphene was initially produced via micromechanical cleavage of graphite using a thin transparent adhesive tape by Novoselov et al.⁴ After that, the development of nanosheets was fast and is still a focus in the research field around the world. There have been many types of nanosheets, obtained one after another. They can be grouped into diverse families, such as the graphene family, 2-D chalcogenides, 2-D oxides, and so on.⁵ The synthesis of the nanosheet can be generally classified into two approaches, “bottom-up” and “top-down.” In “top-down,” micromechanical exfoliation⁴ and liquid exfoliation⁶ are the two common ways; for the “bottom-up” synthesis, two traditional methods, including chemical vapor deposition⁷ and Van der Waal epitaxial growth⁸ are widely used.

Novel physical and chemical properties, such as the quantum size effect⁹ and surface effects,¹⁰ have been gradually revealed for nanosheets. The active component on a nanosheet is completely exposed to its surface.¹¹ In addition, nanosheets can be used as the building blocks to fabricate multifarious nanomaterials.^{12,13} The charge-bearing inorganic macromolecule-like nanomaterials can be assembled or organized through various solution-based processing techniques, including flocculation, electrostatic sequential adsorption, and the Langmuir-Blodgett method.¹⁴

As one kind of nanosheet, HNbWO_6 nanosheet aggregation (e- HNbWO_6) was first realized by Schaak and Mallouk.¹⁵ During the past 13 years, the HNbWO_6 nanosheet has been rapidly developed and applied to different kinds of acid catalytic reactions.^{16–18} But its application in the

*Address all correspondence to: Jie He, E-mail: jhe@aust.edu.cn

photocatalytic field has hardly been reported until now. This study is one of the earliest to apply HNbWO_6 nanosheets to the photocatalytic field. It not only enriches the photocatalyst family further but also has important guiding significance for the preparation and application of HNbWO_6 nanosheet-based nanocomposites such as 2D–0D, 2D–1D, and 2D–2D nanocomposites. In addition, it probably has the greatest advantage for facilitating environmental friendliness.

In the present study, e- HNbWO_6 is prepared by an exfoliation-assembly process. The structures and properties of the as-prepared materials were characterized by means of x-ray diffraction (XRD), scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM), Brunauer–Emmett–Teller (BET), laser Raman spectroscopy (LRS), and ultraviolet-vis diffuse reflectance spectroscopy technology. The photocatalytic performances of the as-prepared samples for degradation of organic pollutants were investigated using methylene blue (MB) as a model substrate.

2 Experimental Section

2.1 Preparation of the Materials

HNbWO_6 was prepared by ion-exchange of LiNbWO_6 , which was synthesized by a solid-state reaction of the stoichiometric mixture of Li_2CO_3 , Nb_2O_5 , and WO_3 with a molar ratio of 1:1:2 at 760°C for 72 h, in a 2 M HNO_3 aqueous solution at 323 K for 96 h; fresh acid solution was replaced every 24 h during the reaction process. Finally, the suspension was separated and the powder was washed with distilled water and dried in air at 353 K overnight.

The HNbWO_6 nanosheet sol was prepared by the liquid exfoliation method of HNbWO_6 using 25% tetrabutylammonium hydroxide (TBA^+OH^-). A suspension was obtained after shaking for 1 week. After centrifugation at a speed of 9000 rpm for 10 min to remove the particles without exfoliation, the supernatant solution containing the dispersed nanosheets was collected. The addition of HNO_3 aqueous solution (0.2 M) to the nanosheet sol resulted in immediate aggregation of the nanosheet as a precipitate. The aggregated HNbWO_6 nanosheet sample was then rinsed three times with distilled water to remove HNO_3 and dried by vacuum technology at 333 K.

2.2 Characterization

The XRD patterns were collected on an XD-3 powder diffractometer (Beijing Purkinje General Instrument Co., Ltd.) using monochromatized $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation under 36 kV and 40 mA. The SEM images were obtained by a Hitachi TM-1000 SEM (Hitachi Ltd.) with an acceleration voltage of 200 kV. The HRTEM microphotographies were captured using a JEOL 2010 (JEOL Ltd.). LRS were obtained by using a confocal Raman microscope spectrometer (InVia Reflex Spectrometer System, Renishaw) with a 532-nm laser at 5-mW laser power. UV-vis diffuse reflectance spectra of the samples were determined on a TU-1901 (Beijing Purkinje General Instrument Co., Ltd.) spectrometer with an integrating sphere assembly and BaSO_4 as a reference sample. Nitrogen adsorption-desorption measurements were conducted at 77.35 K on a NOVA 2000e (Quantachrome Ltd.) specific surface and pore size analyzer. The BET surface area was estimated using adsorption data.

2.3 Photocatalytic Performance Test

Photocatalytic performances of the as-prepared samples were evaluated by the photocatalytic degradation of MB under UV light with a dominant wavelength of 365 nm. In the experiment, 50 mg of the photocatalyst was added to 100 mL of MB solution (5×10^{-5} M). Before illumination, the suspensions were magnetically stirred in the dark for 4 h to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and MB. Then the solution was exposed to UV light irradiation under magnetic stirring. At given time intervals, 3 mL of suspension was sampled and centrifuged to remove the photocatalyst particles. Then the UV-vis

adsorption spectrum of the centrifuged solution was recorded using a Hitachi U-3010 UV-vis spectrophotometer.

3 Results and Discussion

3.1 Structural Features of the As-Prepared Samples

The phase and composition of the as-prepared products were investigated by XRD and the results were shown in Fig. 1.

As shown in Figs. 1(a) and 1(b), all diffraction peaks can be indexed to tetragonal α -LiNbWO₆ and HNbWO₆ according to the JCPDS 41-0378 and 41-0110, respectively. They showed the obvious layered structure, and their interlayer spacings were 0.930 and 1.288 nm, respectively. After exfoliation-assembly, the peak strength of e-HNbWO₆ was significantly weakened and its crystallinity was decreased, but its diffraction pattern was basically identical with that of HNbWO₆. This indicated that the plate-like structure was not destroyed. The (002) plane diffraction peak changed from 6.86 to 5.59 deg, namely, the interlayer spacing was 1.580 nm, which was due to the increase of the hydration degree between the interlayers.

SEM images of as-prepared samples were shown in Fig. 2. As shown in Fig. 2(b), after exfoliation-assembly, the crystallinity of e-HNbWO₆ was decreased to some extent, but the lamellar accumulated structure was distinct and regular. It was in conformity with the XRD results.

Further, the HRTEM microphotographies of e-HNbWO₆ were illustrated in Fig. 3 in which the lamellar accumulated structure was observed. It further confirmed the results of XRD and SEM.

Figure 4 showed the N₂ adsorption-desorption isotherms of HNbWO₆ and e-HNbWO₆. Their isotherm types were categorized as type IV and type III, and they displayed a type H3 hysteresis loop and a type H2 hysteresis loop in the p/p_0 range of 0.995, respectively. The type H3 hysteresis loop suggests the presence of open slit-shaped mesopores with narrow necks, tablet slit structures, fractures, and wedge structures included. However, the type H2 hysteresis loop of e-HNbWO₆ demonstrates that open slit-shaped mesopores of HNbWO₆ changed results from its crystallization, which was shown in Fig. 2(b). The specific surface area of HNbWO₆ was determined to be 7.2 m² g⁻¹, whereas that of e-HNbWO₆ was about 156.5 m² g⁻¹. The significant specific surface area increase may be ascribed to exfoliation of e-HNbWO₆. At the same time, it also proves the surface effect of nanosheets.

Fig. 1 X-ray diffraction patterns of the as-prepared samples: a— α -LiNbWO₆, b—HNbWO₆·nH₂O, and c—e-HNbWO₆.

Fig. 2 Scanning electron microscope images of the as-prepared samples: (a) HNbWO₆ and (b) e-HNbWO₆.

Fig. 3 High-resolution transmission electron microscopy images of the e-HNbWO₆.

Fig. 4 N₂ adsorption-desorption isotherm of the as-prepared samples: a—HNbWO₆ and b—e-HNbWO₆.

3.2 Skeleton Characteristics of the As-Prepared Samples

Raman spectra of LiNbWO₆, HNbWO₆, and e-HNbWO₆ were shown in Fig. 5, and typical absorption peaks and their attributions are listed in Table 1.

As can be seen from Fig. 5 and Table 1, Raman high-frequency peaks (850 to 1000 cm⁻¹) are attributed to the metal-oxygen terminal vibrations. In the Raman spectra, the evolution of the Nb = O and W = O band wave numbers can be explained by the replacement of Li⁺ by H₃O⁺. The peaks observed for all the compounds from about 800 to 400 cm⁻¹ correspond to ν(M-O) vibrations. The peaks displayed at low frequencies (400 to 100 cm⁻¹) corresponded to the bending vibration of M-O or MO₆. When Li⁺ in the host LiNbMoO₆ was exchanged by H⁺ ions, the band corresponded to the stretching vibration of M = O and M-O, and the bending vibration of M-O had changed to a certain extent. This indicated that the effect of interlayer cations on the

Fig. 5 Raman spectra of the as-prepared samples: a—LiNbWO₆, b—HNbWO₆, and c—e-HNbWO₆.

Table 1 Peak position (ν/cm^{-1}) and its attribution of Raman spectra.

Assignment	α -LiNbWO ₆	HNbWO ₆	e-HNbWO ₆	Ref.
$\nu(\text{W}=\text{O})$	954.8	988.6	990.6	19 and 20
$\nu(\text{Nb}=\text{O})$	885.2	904.7	910.0	21
$\nu(\text{W-O-W})$	780.6	808.2	807.3	20
$\nu(\text{Nb-O-W})$	589.4	586.1	592.5	22
$\nu(\text{O-Nb-O})$	447.1	457.3	472.7	23
$\delta(\text{WO}_6)$	406	364.7	365.1	24
$\delta(\text{W-O-Nb})$	288.5	279.8	279.5	25
$\delta(\text{O-Nb-O})$	241.4	229.2	226.1	22 and 26
$\delta(\text{NbO}_6)$	178.3	158.1	159.8	27

skeleton property of the as-prepared samples is significant. It is worth mentioning that the high-frequency peaks had been blue shifted and the low-frequency peaks had been red shifted after being exchanged. Compared with the Raman spectroscopy of HNbWO₆, there had been little change during the exfoliation-assembly process because the interlayer cation had no change during the process.

3.3 Spectral Response Features of the As-Prepared Samples

The UV-vis diffuse reflectance spectra and the band-gap energy of LiNbWO₆, HNbWO₆, and e-HNbWO₆ were shown in Fig. 6. Their absorption edges are 410.6, 396.2, and 392.4 nm; the band gap energies are 3.02, 3.13, and 3.16 eV, respectively. One can find that the band gap energies have just a little change because the plate-like structure had no change. In addition, the band gap of e-HNbWO₆ was broadened slightly. This was attributed to the quantum size effect of the nanosheets.

3.4 Adsorption and Photocatalytic Oxidation Performance of As-Prepared Samples for Methylene Blue

The photocatalytic performances of HNbWO₆ and e-HNbWO₆ were evaluated by the degradation of MB dye in water under UV light using a 500 W-Hg lamp. First, the adsorption of MB

Fig. 6 UV-vis diffuse reflectance spectra of the as-prepared samples. The inset indicates the relationships between $[F(R)hv]^{1/2}$ and photon energy ($h\nu$): a—LiNbWO₆, b—HNbWO₆, and c—e-HNbWO₆.

reached adsorption equilibrium for 4 h under dark so as to exclude the effects of the catalyst surface adsorption rate and the mass transfer processes for a light degradation rate. The temporal UV spectral changes of the MB aqueous solution during the photocatalytic degradation reactions are shown in Fig. 7.

As shown in Fig. 7, the adsorption of MB on the samples has reached adsorption equilibrium under dark conditions for 2 h. The adsorption capacity of MB on HNbWO₆ was 30% and on e-HNbWO₆ was 40% during the dark treatment. This indicates that the adsorption performance of MB on the samples is good enough. As shown in Fig. 7(a), the MB solution was irradiated with UV light in the presence of a blank, HNbWO₆, and e-HNbWO₆. By comparison, catalysts have excellent photocatalytic degradation of MB. The degradation rate of MB on HNbWO₆ and e-HNbWO₆ is 62.5 and 78.5%, respectively. The degradation rate of MB on e-HNbWO₆ is higher than it on HNbWO₆. Figure 7 also shows that the degradation rate of MB on e-HNbWO₆ is 74.2% under UV irradiation for just 20 min. It is generally acknowledged that the adsorption capacity of a degradation object is closely related to the pore volume and pore diameter of the catalyst. However, a larger pore diameter is mainly attributed to the mass transfer processes.

Fig. 7 The degradation rate curve of the photocatalytic degradation of methylene blue: a—blank, b—HNbWO₆, and c—e-HNbWO₆.

4 Conclusions

2D e-HNbWO₆ was obtained by exfoliation of protonated layered LiNbWO₆. The layered structure of e-HNbWO₆ was affected to a certain extent, but the interlayer space of e-HNbWO₆ was increased; the surface area increased nearly 30 times compared to HNbWO₆, and the skeleton structure of e-HNbWO₆ retained its integrity. The photocatalytic activity is enhanced significantly after the exfoliation-assembly. Herein, the pore structure and surface area of e-HNbWO₆ played an important role; the e-HNbWO₆ surface with abundant hydroxyl radicals contributed to promote the reaction activity under UV irradiation.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos. 21271008 and 21071004).

References

1. E. A. Hauser and C. E. Reed, "Studies in thixotropy. I. Development of a new method for measuring particle-size distribution in colloidal systems," *J. Phys. Chem.* **40**(9), 1169–1182 (1936).
2. E. A. Hauser and C. E. Reed, "Studies in thixotropy. II. The thixotropic behavior structure of bentonite," *J. Phys. Chem.* **41**(7), 911–934 (1937).
3. T. Sasaki et al., "Macromolecule-like aspects for a colloidal suspension of an exfoliated titanate. Pairwise association of nanosheets and dynamic reassembling process initiated from it," *J. Am. Chem. Soc.* **118**(35), 8329–8335 (1996).
4. K. S. Novoselov et al., "Electric field effect in atomically thin carbon films," *Science* **306**(5696), 666–669 (2004).
5. A. K. Geim and I. V. Grigorieva, "Van der Waals heterostructures," *Nature* **499**, 419–425 (2013).
6. A. Gupta, T. Sakthivel, and S. Seal, "Recent development in 2D materials beyond graphene," *Prog. Mater. Sci.* **73**, 44–126 (2015).
7. Y. Zhang, L. Zhang, and C. Zhou, "Review of chemical vapor deposition of graphene and related applications," *Acc. Chem. Res.* **46**(10), 2329–2339 (2013).
8. Z. Sun et al., "Generalized self-assembly of scalable two-dimensional transition metal oxide nanosheets," *Nat. Commun.* **5**, 3813 (2014).
9. K. Fukuda et al., "Exfoliated nanosheet crystallite of cesium tungstate with 2D pyrochlore structure: synthesis, characterization, and photochromic properties," *ACS Nano* **2**(8), 1689–1695 (2008).
10. Y. Bai et al., "Porous titania nanosheet/nanoparticle hybrids as photoanodes for dye-sensitized solar cells," *ACS Appl. Mater. Interfaces* **5**(22), 12058–12065 (2013).
11. J. Xie et al., "Atomically-thin molybdenum nitride nanosheets with exposed active surface sites for efficient hydrogen evolution," *Chem. Sci.* **5**, 4615–4620 (2014).
12. M. A. Bizeto, A. L. Shiguiharab, and V. R. L. Constantino, "Layered niobate nanosheets: building blocks for advanced materials assembly," *J. Mater. Chem.* **19**, 2512–2525 (2009).
13. J. L. Gunjekar et al., "Exploration of nanostructured functional materials based on hybridization of inorganic 2D nanosheets," *J. Phys. Chem. C* **118**(8), 3847–3863 (2014).
14. R. Ma and T. Sasaki, "Nanosheets of oxides and hydroxides: ultimate 2D charge-bearing functional crystallites," *Adv. Mater.* **22**, 5082–5104 (2010).
15. R. E. Schaak and T. E. Mallouk, "Exfoliation of layered rutile and perovskite tungstates," *Chem. Commun.* **7**, 706–707 (2002).
16. G. K. Prasad et al., "Nanocomposites based on exfoliated NbWO₆ nanosheets and ionic polyacetylenes," *Solid State Ionics* **177**(1–2), 197–201 (2006).
17. G. K. Prasad et al., "Hybrid nanocomposite based on NbWO₆ nanosheets and polyaniline," *Mater. Lett.* **60**, 3727–3730 (2006).
18. C. Tagusagawa et al., "Characterization of HNbWO₆ and HTaWO₆ metal oxide nanosheet aggregates as solid acid catalysts," *J. Phys. Chem. C* **113**(18), 7831–7837 (2009).

19. L. Shi, B. Li, and L. Wu, "Polyoxometalates as inorganic chiral ligands for the synthesis of chiral nanoparticles," *Chem. Commun.* **51**, 172–175 (2015).
20. Y. Kong et al., "Fabrication of hexagonal/cubic tungsten oxide homojunction with improved photocatalytic activity," *Appl. Catal. A-Gen.* **505**(25), 447–455 (2015).
21. T. Murayama et al., "Hydrothermal synthesis of octahedra-based layered niobium oxide and its catalytic activity as a solid acid," *Catal. Sci. Technol.* **4**, 4250–4257 (2014).
22. S. Wan et al., "Structural analyses of a K_2O -rich $KNbO_3$ melt and the mechanism of $KNbO_3$ crystal growth," *CrystEngComm* **17**(13), 2636–2641 (2015).
23. S. M. Hsu et al., "Evaluation of chemical durability, thermal properties and structure characteristics of Nb-Sr-phosphate glasses by Raman and NMR spectroscopy," *J. Non Cryst. Solids* **358**(1), 14–19 (2012).
24. S. D. Ramarao and V. R. K. Murthy, "Structural, Raman spectroscopic and microwave dielectric studies on $Ni_{1-x}(Zn_{1/2}Zr_{1/2})_xW_{1-x}Nb_xO_4$ ceramic compounds with wolframite structure," *Dalton Trans.* **44**(5), 2311–2324 (2015).
25. J. Yan et al., "Tungsten oxide single crystal nanosheets for enhanced multichannel solar light harvesting," *Adv. Mater.* **27**, 1580–1586 (2015).
26. D. Xu et al., "Optical phonon behaviors of columbite $ZnNb_2O_6$ single crystal," *J. Alloys Compd.* **618**, 694–699 (2015).
27. N. Ushaa et al., "Niobium pentoxide (Nb_2O_5) thin films: rf power and substrate temperature induced changes in physical properties," *Optik Int. J. Light Electron Opt.* **126**, 1945–1950 (2015).

Li-Fang Hu graduated from Anhui University of Science and Technology with a Bachelor of Engineering in 2012 and with a Master of Engineering in industrial catalysis in 2015. Currently, he is a PhD student in environmental engineering, supervised by Professor Jie He. His research interests include the construction and catalytic properties of solid acid catalysts and nanoscale photocatalysts.

Rui Li graduated from Yunnan Normal University with a Bachelor of Engineering in 2010 and from Anhui University of Science and Technology with a Master of Engineering in industrial catalysis in 2013. Her research interests include the construction and application of nanocomposites.

Jie He is a professor of Anhui University of Science and Technology. He received his PhD (2004) and BSc (1990) degree from Nanjing University, China. He was a postdoctoral research fellow from 2005 to 2006 in University of Yamanashi, Japan. His current focus is on inorganic functional materials, environmental catalysis, catalytic chemical, and surface or interface chemistry.

Liang-guo Da graduated from the University of Science and Technology of China with a Master of Engineering in industrial catalysis. Currently, he is a PhD student in environmental engineering, supervised by Professor Jie He. His research interests include the construction, quantum computation, and application of nanoscale photocatalysts.

Wei Lv graduated from Anhui University of Science and Technology with a Bachelor of Engineering in 2014. Currently, he is an MS student in industrial catalysis, supervised by Professor Jie He. His research interests include the doping modification and application of composite metal oxides.

Jin-song Hu is an associate professor of Anhui University of Science and Technology. He graduated from Anhui Normal University with a Master of Science (2008). He received his PhD in chemistry from Nanjing University in 2011 and he is currently a postdoctoral fellow at KAUST. His current focus is on functional coordination polymer chemistry, metal clusters chemistry and so on.