

Synthesis and optical property of size-tunable vanadium oxide nano-dandelions

Chaojiang Niu, Chunhua Han, Yunlong Zhao, Xiaocong Tian, Wanli Guo, Yanhui Gu, Liqiang Mai*

WUT-Harvard Joint Nano Key Laboratory,
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,
Wuhan University of Technology, Wuhan, 430070, China

*Author for correspondence: Liqiang Mai, email: mlq518@whut.edu.cn
Received 19 Oct 2012; Accepted 12 Nov 2012; Available Online 12 Nov 2012

Abstract

One-dimensional vanadium oxides with desired physical and chemical properties have attracted great attentions in nanoelectronics, nanooptoelectronics and energy storage and so on. Here we controllably synthesized size-tunable dandelion-like vanadium oxides through a flexible microemulsion approach. The detailed assembly process of the vanadium oxides nano-dandelion was investigated by controlling the reactant concentration and aging time. The nano-dandelions were composed of vanadium oxides nanorods with small size. The self-organizational structure can be changed from dandelion-like structure to side-by-side alignment and bunchy-like structure. Such novel vanadium oxide nano-dandelions show good photoluminescence property and may have great potential application in luminescence and other fields.

Keywords: Dandelion-like vanadium oxide; Microemulsion; Assembly process; Photoluminescence

1. Introduction

Recently, an increasing attention has been attracted for one-dimensional (1D) nanomaterials due to their special electrical, optical, chemical, magnetic, thermal and other performance [1] and various synthetic strategies can be used to obtain one-dimensional nanomaterials [2]. With high anisotropic crystal structures, 1D nanomaterials exhibit excellent performance in the field of nanoelectronics, nanooptoelectronics, energy storage, healthcare and so on [2-4]. However, the design of one-dimensional nanomaterials with high-quality monodispersed, desired shape and structure has been investigated intensively in recent years but still remains a challenge [5-7]. Specially, novel self-organizational structure of 1D nanomaterials has been rarely reported [8-10]. 1D vanadium oxides, including nanorods [11-13], nanotubes [14-16], nanowires [17, 18], nanobelts [19, 20] and nanofibers [21], are of intense interest and have been extensively investigated as important transition-metal oxides. However, there are few studies focused on the controlled self-organizational structure [22] and photoluminescence property of 1D vanadium oxides.

On the other hand, transition metal oxides have been extensively studied over the past decade [23]. Vanadium oxides, known as transition metal oxide and wide band gap semiconductor material, have gained great interests for Li-ion batteries, supercapacitors, photoelectric device and so on [23, 24]. High performance of vanadium oxide nanomaterials can be constructed through structure assembly [24].

In this work, by using water-in-oil microemulsions system, the vanadium oxides nanorods with controllable size and the dandelion-like organizational structure can be synthesized by changing the reactant concentration and aging time. In a typical synthesis, a certain volume of ammonia was added into VOSO₄ microemulsion, to give final molar ratios of [NH₄⁺]: [SO₄²⁻] = 2 and water content [H₂O]: [SDS] = 16.

2. Experimental Details

2.1. Materials

VOSO₄ (≥98%), sodium dodecyl sulfate (SDS) (≥99%), cyclohexane (≥99%), normal butanol (≥99%), NH₃•H₂O (≥99.7%), sooctane (≥99%), alcohol (≥99.7%)

2.2. Synthesis of vanadium oxide nano-dandelion

Size-tunable vanadium oxide nano-dandelions were prepared by micro-emulsion method with VOSO₄ and NH₃•H₂O, SDS, and VOSO₄ were dispersed in 40 mL cyclohexane as mother solution. With stirring, 7 mL normal butanol was added into the mother solution to form the microemulsion. After stirring for 1 h, 1 mL 9 mol/L NH₃•H₂O was added into the microemulsion and stirring was stopped until solution turned into black. After aging, the sample was washed with deionized water and ethanol, and dried for further characterization.

2.3. Characterization

Scanning electron microscopy (SEM) performed on JSM-5610LV was used to characterize the morphology of the synthesized nano-materials. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) was recorded by using a JEOL JEM-2010 FEF microscope at an accelerating voltage of 200 kV. Photoluminescence was measured using RF-5301PC SHIMADZU.

3. Results and Discussion

Figure 1a, b, c, d show the morphology of products synthesized by controlling the concentration of VOSO₄ for 0.9 M and aging for 1 d, 2 d, 4 d, 5 d, respectively. It reveals the growth process of vanadium oxide nano-dandelion. At the first step of reaction, vanadium oxide nanoparticles were formed as

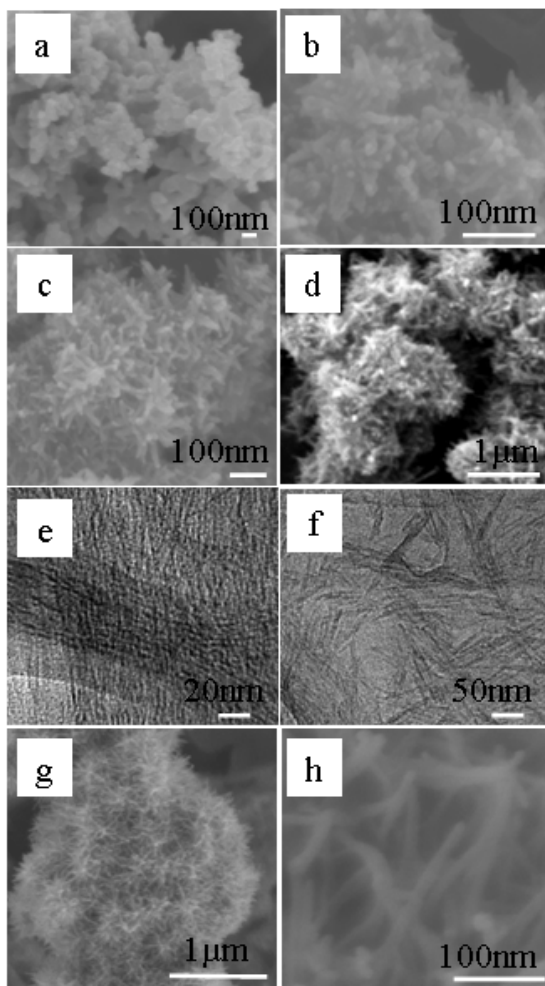


Figure 1. SEM images of product synthesized by controlling the concentration of VOSO_4 for 0.9 M and aging for 1 d (a), 2 d (b), 4 d (c); TEM images of product synthesized by controlling the concentration of VOSO_4 for 0.9 M and aging for 5 d: dispersed in chloroform (e) and ethanol (f), respectively; Low-magnification (g) and high-magnification (h) SEM images of typical vanadium oxides nano-dandelion prepared by controlling the concentration of VOSO_4 for 2 M and aging for 5 d.

shown in Figure 1a. With continuous reaction, nanoparticles grew into nanorods gradually and imperfect nano-dandelions with diameter about 0.3-0.5 μm were self-assembled. Figure 1b shows that the nanoparticles and nanorods coexist. After aging for 4 d, perfect nano-dandelions with diameter about 0.5-0.8 μm were formed as shown in Figure 1c. All of the dandelions are composed of nanorods. After aging for 5 d, the dandelions expand to about 1 μm as shown in Figure 1d. Further information about nano-dandelions were obtained by TEM. These nano-dandelions are composed of monodispersed quantum rods with uniform size, diameter about 2-5 nm and length about 100-200 nm (Figure 1e). The ultra-narrow rods dispersed in chloroform are self-assembled into 2D supercrystalline arrays without any postsynthesis treatment by putting a drop of suspension from a microsyringe onto a transmission electron microscopy (TEM) grid, maintaining the ultra-narrow width and tight side-by-side registry by directional capillary force and van der Waals attraction [25]. The center-to-center lateral distance (pitch) between the nanorods is measured to be 5 nm. However, the size of nanorods dispersed in ethanol (Figure 1f) seems to be larger than that dispersed in chloroform, and the directions of rods

are isotropically distributed. The ultra-narrow rods were self-assembled to bundle-like structure in ethanol. The existence of strong attractive interactions among the rods would complicate their assembly process [26]. The van der Waals attraction term is given by equation:

$$V_A(r) = -\frac{A}{6} \left[\frac{2R^2}{r^2 - 4R^2} + \frac{2R^2}{r^2} + \ln \left(1 - \frac{4R^2}{r^2} \right) \right]$$

While the particle radius R is determined by nanorods and the distance r between two separate particles. r is determined by the concentration and dispersion of nanorods. The Hamaker constant A is given by equation:

$$A = \left(\frac{\rho N_A}{M} \right)^2 \pi^2 \beta = \frac{3}{4} h\nu\pi^2 \left(\frac{\rho N_A}{M} \right)^2 \left(\frac{\alpha}{4\pi\epsilon_0} \right)^2$$

ρ , M are determined by the properties of the particles and α is determined by suspension mediums, in particular their frequency-dependent polarizabilities. Hence, the van der Waals attraction in different suspension medium depends on the polarizability of solvent. Meanwhile, the polarizability of ethanol and chloroform is 24.3 and 4.81, respectively. The magnitude difference of polarizabilities between the two solvents maybe is the main factor for the different assembly behavior. 1D nanomaterials with different aspect ratios can form different superstructures such as raftlike, ribbonlike, side by side and crossed haystack [26-29]. For ultra-narrow vanadium oxide quantum rods, such supercrystalline array is formed due to the higher lateral capillary forces along the length of a rod as compared to its width. This anisotropy of interaction between the rods could be one important driving force for the side-by-side, rather than end-to-end, alignment of rods. However, the dispersibility of nanorods is relatively worse in ethanol than chloroform, which results in aggregation of the nanorods to bundle-like structure. Considering the effect of the concentration of VOSO_4 , the vanadium oxides nano-dandelions with larger size were prepared by controlling the concentration of VOSO_4 for 2 M, aging for 5 days (Figure 1g, 1h). The diameter of nano-dandelion is about 2 μm . Tens of size-uniform nanorods with diameter about 13 nm were self-assembled to a small petal. A lot of petals organized a dandelion via the secondary-assembly.

Based on the morphology under different growing times and the structure characteristic of vanadium oxide nano-dandelions, the assembly process of dandelion can be illustrated in Figure 2. In the microemulsion system, the hydrophilic group of the SDS points to the water pool while the hydrophobic end points to the outer. When the Na^+ ions is ionized in water, VO^{2+} ions with higher electrovalence are absorbed by the sulfonic group of SDS because of the electrostatic interaction, which make the interface of water and oil occupied by numerous VO^{2+} cations (step 1). While the NH_4OH molecules diffuse into water pool, the vanadium oxides nuclei are formed (step 2). During the process of aging, vanadium oxides nanorods grow along a certain direction because of the inducement of SDS, crossing each other to assemble a small petal of dandelion (step 3) and form a dandelion via secondary-assembly (step 4). Because that the size of nanorods is small enough and nanorods can be dissolved in organic solvent such as chloroform and ethanol to form colloidal suspension but cannot be dissolved in water, we

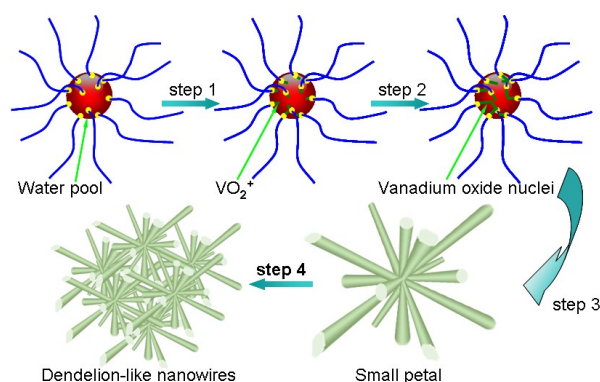
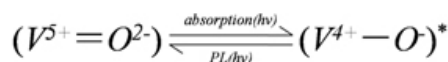


Figure 2. Schematic illustration of assembly process of the vanadium oxides nano-dandelion.

deduce that the driving force of secondary-assembly is the interfacial tension and hydrophobic interaction of nanorods [30].

The photoluminescence (PL) spectrum of the vanadium oxide nano-dandelion dispersed in chloroform, which was synthesized by controlling the concentration of VOSO_4 for 0.9 M and aging time 5 d, is shown in Figure 3. The PL spectrum of vanadium oxide nanomaterial was seldom reported and largely unexplored. The V^{4+} and V^{5+} coexist in vanadium oxides with mixed-valence. To our knowledge, the luminescent mechanism at 423 nm was caused by the electric charge transfer, corresponding to the weak energy of $\text{V}=\text{O}$ bond. These processes involve an electron transfer from O^{2-} to V^{5+} and a reverse radiative decay from the charge transfer excited triplet state [31]. The charge transfer equation is:



The peak at 399 nm and 331 nm may be attributed to free-excitation emission and bound-excitation emission, respectively [32]. Commonly, the smaller the size of nanomaterial, the more are the oxygen vacancies. The bound-excitation mainly roots in large numbers of oxygen vacancy on the surface of quantum-sized vanadium oxide rods [33, 34]. The shoulder peak at 440 nm may be caused by defect energy gap [35, 36]. The further research about the PL property of nanorods is in process.

4. Conclusions

In summary, by using a flexible microemulsion method, different sizes of vanadium oxide nano-dandelions were obtained by controlling the aging time and the concentration of VOSO_4 . The nano-dandelions were composed of vanadium oxides nanorods with small size. The self-organizational structure can be changed from dandelion-like structure to side-by-side alignment and bunchy-like structure. The growing process and assembly of nanorods were explained and the PL property of vanadium oxide nanorods was studied. This vanadium oxide with special structure may have potential applications for luminescence materials and other fields.

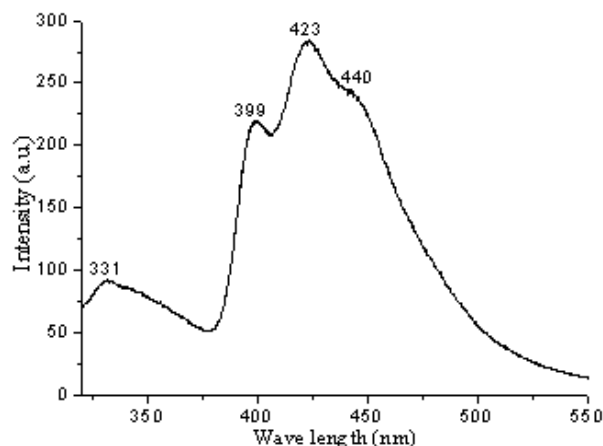


Figure 3. Photoluminescence spectrum of the vanadium oxides nano-dandelion dispersed in chloroform, which was synthesized by controlling the concentration of VOSO_4 0.9 M and aging time 5 d.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51072153, 51272197), the Program for New Century Excellent Talents in University (NCET-10-0661), the National Basic Research Program of China (2013CB934103, 2012CB933003) and the Fundamental Research Funds for the Central Universities (2012-II-001, 2011-II-012).

References

1. C. M. Lieber and Z. L. Wang, *MRS Bull.* 32 (2007) 99.
2. X. Xu, Y. Z. Luo, L. Q. Mai, Y. L. Zhao, Q. Y. An, L. Xu, F. Hu, L. Zhang, Q. J. Zhang, *NPG Asia Mater.* 4 (2012) e20.
3. M. S. Whittingham, *Chem. Rev.* 104 (2004) 4271.
4. L. Q. Mai, F. Yang, Y. L. Zhao, X. Xu, L. Xu, B. Hu, Y. Z. Luo and H. Y. Liu, *Mater. Today* 14 (2011) 346.
5. Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science* 291 (2001) 1947.
6. Satyanarayana V. N. T. Kuchibhatla, A. S. Karakoti, Debasish Bera, S. Seal, *Prog. Mater. Sci.* 52 (2007) 699.
7. Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, Y. Q. Yan, *Adv. Mater.* 15 (2003) 353.
8. X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature* 437 (2005) 121.
9. Z. Liu, D. Zhang, S. Han, C. Li, B. Lei, W. Lu, J. Fang, C. Zhou, *J. Am. Chem. Soc.* 127 (2005) 6.
10. M. Cao, C. Hu, G. Peng, Y. Qi, E. Wang, *J. Am. Chem. Soc.* 125 (2003) 4982.
11. G. Zhou, F. Rong, W. Mo, X. Chen, Y. Ling, S. Zhang, Y. Hu, Z. Wang, and W. Fan, *Chem. Mater.* 14 (2002) 5053.
12. O. Rainer, L. Dan, Y. Yin, Jesse T. McCann, and Y. Xia, *Nano Lett.* 6 (2006) 1297.
13. A. Cao, J. Hu, H. Liang, and L. Wan, *Angew. Chem. Int. Ed.* 44 (2005) 4391.
14. J. Shyue and Mark R. De Guire, *J. Am. Chem. Soc.* 127 (2005) 12736.
15. Y. Wang, K. Takahashi, H. Shang, and G. Cao, *J. Phys. Chem. B* 109 (2005) 3085.
16. F. Krumeich, H. J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, and R. Nesper, *J. Am. Chem. Soc.* 121 (1999) 8324.
17. Y. Chang, B. H. Kang, G. T. Kim, S. J. Park, J. S. Ha, *Appl. Phys. Lett.* 84 (2004) 5392.
18. C. Mao, H. Pan, X. Wu, J. Zhu, and H. Chen, *J. Phys. Chem. B* 110 (2006) 14709.

19. G. C. Li, S. P. Pang, L. Jiang, Z. Y. Guo, Z. K. Zhang., J. Phys. Chem. B 110 (2006) 9383.
20. C. K. Chan, H. Peng, R. D. Twisten, K. Jarausch, X. F. Zhang, and Y. Cui., Nano Lett. 7 (2007) 490.
21. L. Biette, F. Carn, M. Maugey, M. Achard, J. Maquet, N. Steunou, J. Livage, H. Serier, and R. Backov., Adv. Mater. 17 (2005) 2970.
22. C. O'Dwyer, D. Navas, V. Lavayen, E. Benavente, M. A. Santa Ana, G. González, S. B. Newcomb, and C. M. Sotomayor Torres., Chem. Mater. 18 (2006) 3016.
23. J. Meyer, S. Hamwi, M. Kröger, W. Kowalsky, T. Riedl, A. Kahn, Adv. Mater. 24 (2012) 5408.
24. L. Q. Mai, X. Xu, L. Xu, C. H. Han, Y. Z. Luo, J. Mater. Res. 26 (2011) 2175.
25. F. Kim, S. Kwan, J. Akana, and P. Yang., J. Am. Chem. Soc. 123 (2001) 4360.
26. P. Yang and F. Kim, ChemPhysChem 3 (2003) 503.
27. B. Nikoobakht, Z. L. Wang, and M. A. El-Sayed., J. Phys. Chem. B 104 (2000) 8635.
28. S. Kwan, F. Kim, J. Akana and P. Yang., Chem. Commun. 5 (2001) 447.
29. Patla, S. Acharya, L. Zeiri, J. Israelachvili, S. Efrima, and Y. Golan., Nano Lett. 7 (2007) 1459.
30. J. Yuan, W. Li, S. Gomez and S. L. Suib., J. Am. Chem. Soc. 127 (2005) 14184.
31. M. Anpo, I. Tanahashi, and Y. Kubokawa., J. Phys. Chem. 84 (1980) 3440.
32. M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, Chem. Soc. Rev. 38 (2009) 1330.
33. L. D. Carlos, R. A. S. Ferreira, V. Z. Bermudez, Adv. Mater. 21 (2009) 509.
34. X. Y. Wang, X. F. Ren, K. Kahen, Nature 459 (2009) 7247.
35. D. Y. Pan, J. C. Zhang, Z. Li, Adv. Mater. 22 (2010) 734.
36. C. A. J. Lin, T. Y. Yang, C. H. Lee, ACS Nano 3 (2009) 395.

Cite this article as:

Chaojiang Niu *et al.*: **Synthesis and optical property of size-tunable vanadium oxide nano-dandelion.** *J. Nanosci. Lett.* 2013, **3**: 27