

Rapid communication

Synthesis and characterization of vanadium oxides nanorods

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Abstract

Vanadium oxides nanorods with high crystallinity and high surface area were synthesized by hydrothermal method using laurylamine hydrochloride, metal alkoxide and acetylacetone. The samples characterized by XRD, nitrogen adsorption isotherm, SEM, TEM, and SAED. Uniformly sized B phase VO₂ nanorods had widths about 40–80 nm and lengths reaching up to 1 μm. V₂O₅ rodlike structured with the widths about 100–500 nm and the lengths of 1–10 μm were obtained by calcination at 400 °C for 4 h. This synthesis method provides a new simple route to fabricate one-dimensional nanostructured metal oxides under mild conditions.

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1. Introduction

The synthesis and characterization of one-dimensional (1-D) nanostructured (nanotubes, nanowires, and nanorods) have received considerable attention due to their unique properties and novel application [1–5]. Much effort has concentrated on the important metal oxides such as TiO₂, SnO₂, WO₃, ZnO, and ZrO₂. Among them vanadium oxides are especially interesting since they are widely used for various applications like electrochemical device and catalysis [6–8]. Their functional properties are influenced by many factors such as crystallinity, surface area, and preparation methods [6–13]. A large number of vanadium oxides nanotubes were successfully synthesized via a sol–gel reaction followed by hydrothermal treatment [10–13]. Important progress was achieved in producing nanofibers and

nanotubes of vanadium oxides using carbon nanotubes as template [14,15]. Owing to high cost of carbon nanotubes, the use of titanate nanotubes as template via hydrothermal synthesis (200 °C) was investigated; however, the products were composite of vanadium oxide and titanate nanorods [16]. V₂O₅ nanorods from VOSO₄ aqueous solution using template-based electrodeposition were also successfully synthesized [17]. In our previous works, mesoporous metal oxides nanopowders with controlled pore size (3–6 nm) were synthesized by a modified sol–gel method in aqueous phase using a surfactant assisted process under mild conditions, offering a high photocatalytic activity [18–20]. This process has also been applied to a semiconductive material in dye-sensitized solar cells and hydrogen evolution [21–26].

In this study, the surfactant-assisted process has been expanded to prepare nanostructured vanadium oxides by hydrothermal method. The characteristic of the prepared nanopowders will be reported.

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2. Experimental

2.1. Synthesis

Nanostructured vanadium oxides were synthesized using laurylamine hydrochloride (LAHC)/metal alkoxide modified with acetylacetone (ACA). Vanadium triethoxide oxide (VTO, Hokko Chemical Industry Co., Ltd.) was mixed with the same mole of ACA (Nacalai Tesque, Inc.) to slowdown the hydrolysis and condensation reactions [18,21,25]. Subsequently, 0.1 M LAHC (Tokyo Chemical Industry Co.) aqueous solution (as the surfactant, pH 4–4.5) was added in the solution (molar ratio of VTO to LAHC was 4), and it was stirred at room temperature for 1 h. After kept stirring at 40 °C for 24 h, it was put into a Teflon-lined stainless steel autoclave and heated at 150 °C for 1 week. The obtained black green product was washed with 2-propanol and distilled water, followed by freeze-drying.

2.2. Characterization

The crystalline structure of samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE), transmission electron microscopy (TEM, JEOL JEM-200CX), and selected-area electron diffraction (SAED). The Brunauer–Emmett–Teller (BET) specific surface area was determined by the nitrogen adsorption (BEL Japan, BELSORP-18 Plus). Thermal analytical measurements were carried out on a thermogravimetric analyzer (Perkin Elmer, Pyris 1 TGA). Infrared spectra were obtained with Fourier Transfer Infrared Spectroscopy (FTIR, Perkin Elmer. Spectrum One) using KBr technique.

3. Results and discussion

Fig. 1 shows XRD patterns of the prepared samples. As-synthesized sample was composed of monoclinic B phase VO₂ (JCPDS card No: 31-1438). The peaks were rather sharp, which indicated relatively high crystallinity. Metastable B phase VO₂ was found to have good performance in lithium batteries [27–29]. Nanocrystal B phase VO₂ had been obtained by an ambient temperature reduction of aqueous vanadate ions with potassium borohydride and sodium dithionite followed by heating in vacuum at 230 °C [29]. However, B phase VO₂ nanorods were obtained by this method.

The SEM image (Fig. 2(a)) reveals that the prepared VO₂ without ACA display rodlike morphology with 100–400 nm in width and 500 nm–2 μm in length. The BET surface area was about 28 m²/g. More uniform

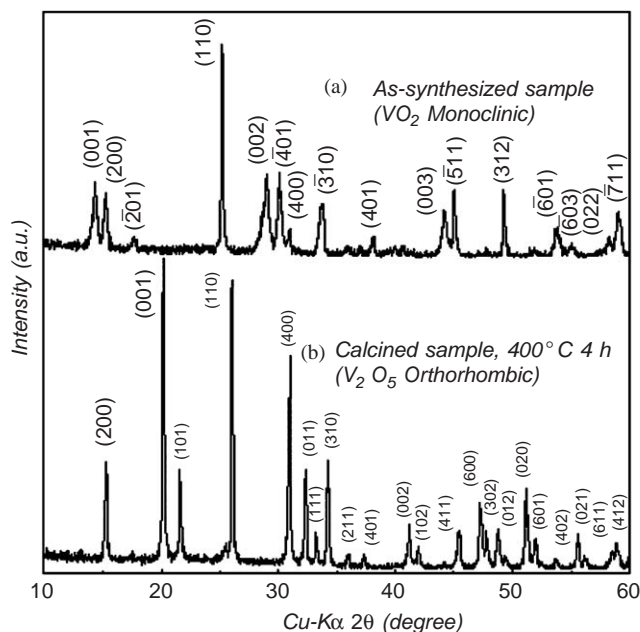


Fig. 1. XRD patterns for (a) the as-synthesized sample, (b) the calcined sample at 400 °C for 4 h.

shape and finer size of nanorods were obtained with ACA addition (Fig. 2(b)).

The widths of rods decreased between 40 and 80 nm, the thickness of 15–50 nm, and the lengths of nanorods range from 500 nm to 1 μm (Fig. 3(a)). Because the condensation reaction speed was much faster under without ACA condition, it is predicted that the crystal growth occurred before the surfactant molecules were adsorbed on the nanostructured vanadium oxide [25]. VO₂ nanorods are frequently grown together in the form of bundles, however individual nanorod can also be observed, which can be confirmed by the HRTEM and SAED investigation. Lattice fringes of 001, 200, and 110 were confirm, (Fig. 3(b–d)) ($d = 0.61, 0.58,$ and 0.35 nm) allowing for the identification of the monoclinic phase. HRTEM images of nanorods with clear lattice fringes, again confirming its high crystallinity.

In order to confirm the essential of LAHC for the nanorods formation, lower molar ratio of VTO to LAHC and other amine surfactant have been used. In the condition of [VTO]/[LAHC] = 1, nano-micro plate-like structured vanadium oxide was obtained (Fig. 4(a)). Without LAHC condition (no surfactant), vanadium oxide nanorods were not obtained (Fig. 4(b)). It can be deduced that lower molar ratio of precursor to surfactant may destroy the dynamic equilibrium of microemulsions, resulting in the loss of microemulsion function [30]. Needle-like nanostructured could be observed with the used of myristylamine as the surfactant condition (Fig. 5(a, b)), however, B phase VO₂ has not been obtained.

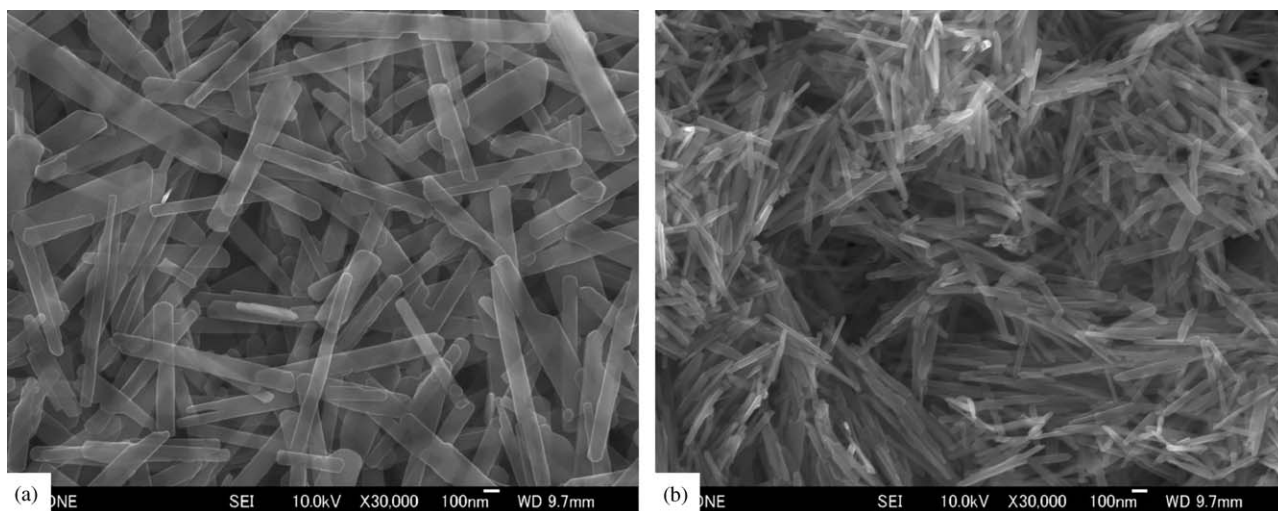


Fig. 2. SEM images of the as-synthesized VO_2 without ACA (a) and with ACA (b) condition.

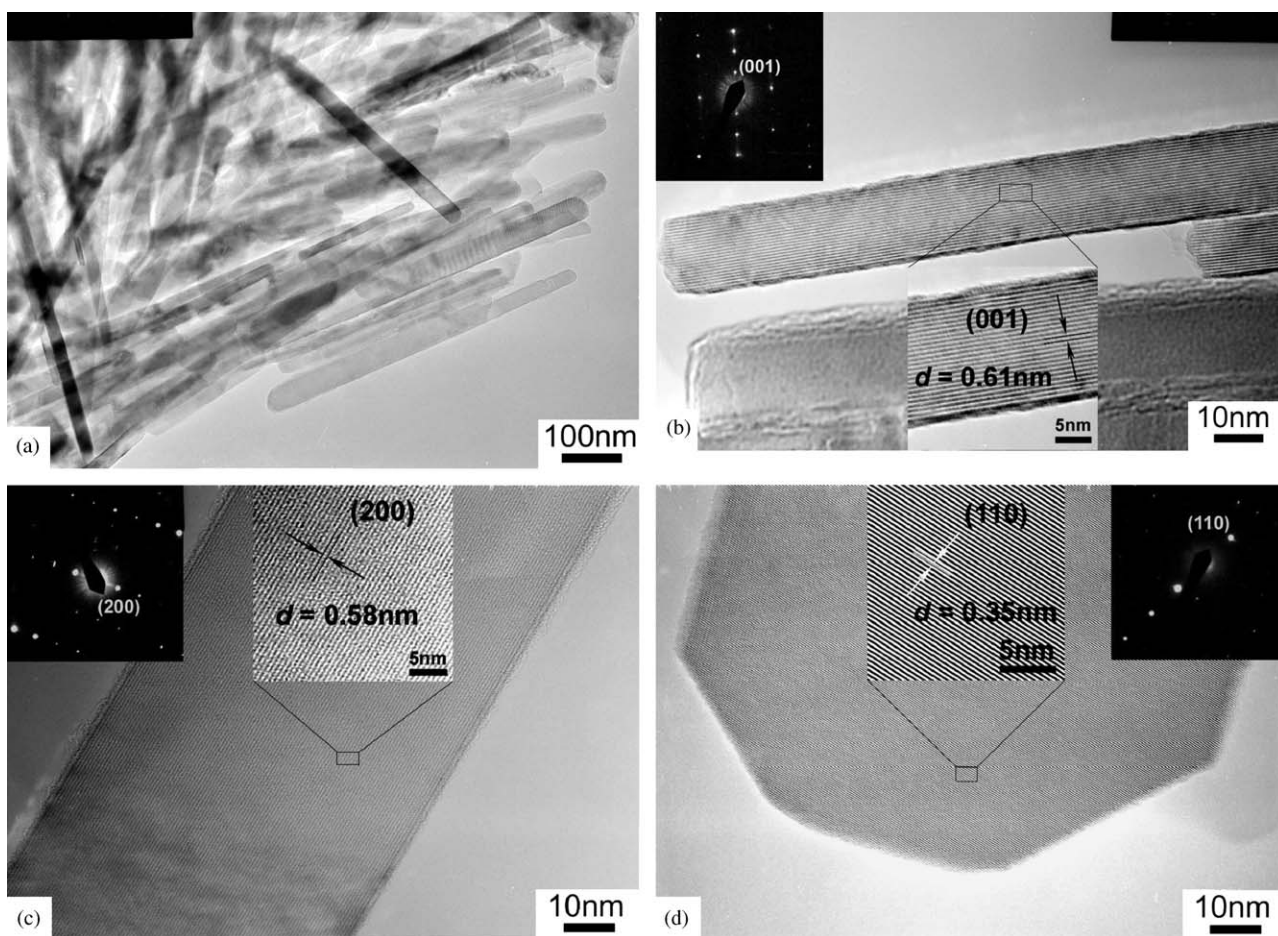


Fig. 3. (a) TEM, (b–d) HRTEM and SAED images of the as-synthesized VO_2 .

The mechanism of this vanadium oxides nanorods synthesis is not very clear yet. Nevertheless, organic molecules such as surfactants act as surface ligands and have the ability to control the shape and size of the

growing particles, as was shown recently by Banfield et al. [31]. We believe that LAHC plays a critical role in this system because the nanorods cannot be obtained under hydrothermal condition without the presence of

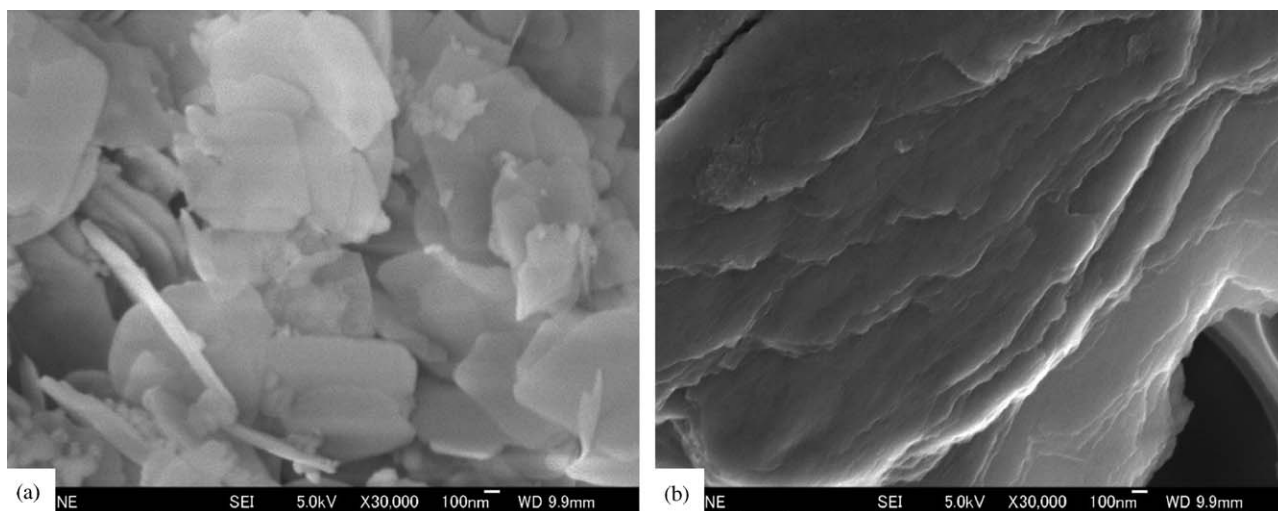


Fig. 4. SEM images of the as-synthesized VO₂ with [VTO]/[LAHC] = 1 condition (a), and the as-synthesized VO₂ without LAHC condition (b).

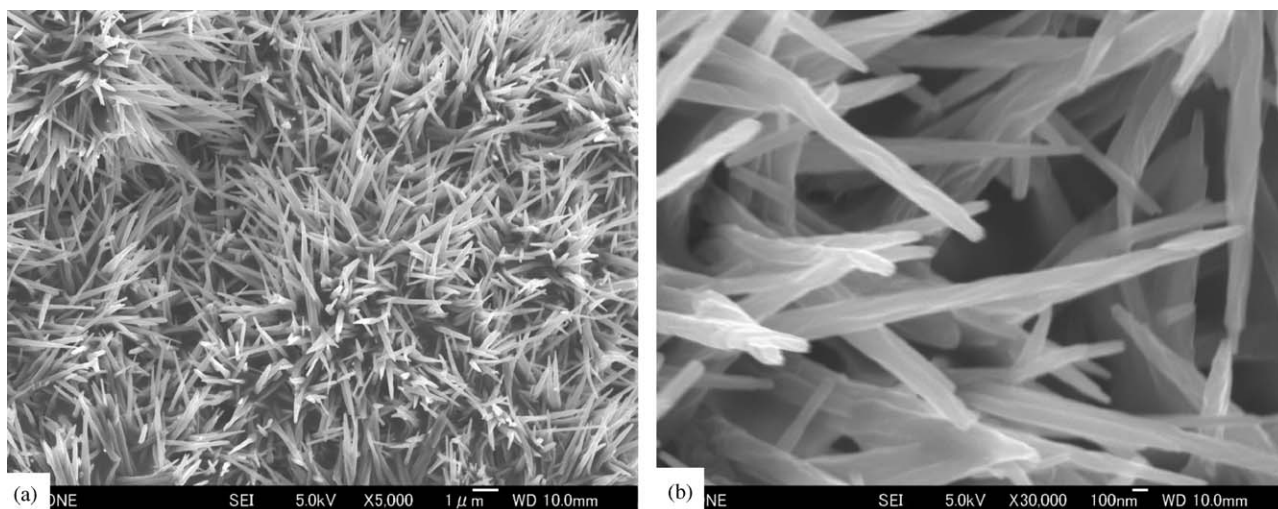
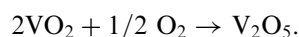


Fig. 5. SEM images of the as-synthesized VO₂ (myristylamine as the surfactant): (a) × 5000 magnified, (b) × 30,000 magnified.

LAHC. It has been recently reported that LAHC and metal alkoxide can form nanorods by oriented attachment mechanism [25].

As shown in Fig 6, TGA test of the as-synthesized VO₂ was conducted simultaneously at a heating rate of 10 °C/min between room temperature and 800 °C (in air 50 ml/min). According to the result, before 380 °C, weight loss corresponds to the decomposition of residual surfactant and the loss of water. There is a sharp exothermic peak at around 380 °C, which should be ascribed to the formation of crystallization of V₂O₅. The oxidation occurred at around 380 and 410 °C. The possible reaction mechanism includes the following reaction [32]:



The XRD patterns (Fig. 1(b)) of powder calcined at 400 °C for 4 h, consisted of orthorhombic V₂O₅ (JCPDS

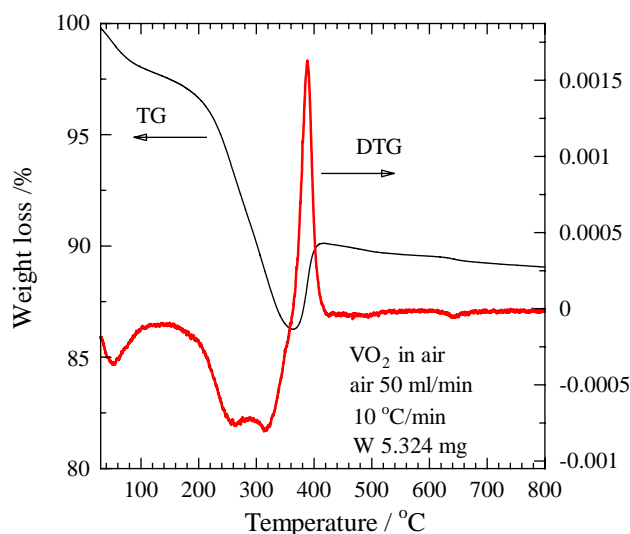


Fig. 6. TGA analyses of the as-synthesized VO₂.

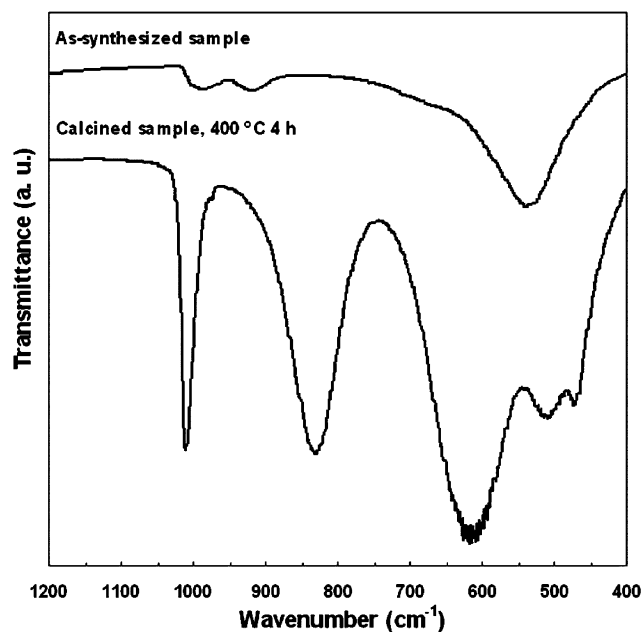


Fig. 7. FTIR spectra for (a) the as-synthesized sample, (b) the calcined sample at 400 °C for 4 h.

card No: 09-387) with high crystallinity. Weight gains caused by the formation of V_2O_5 are demonstrated.

Fig. 7 displays the FTIR spectrum for as-synthesized VO_2 and V_2O_5 calcined at 400 °C for 4 h. The 995–1000 cm^{-1} band observed for B phase VO_2 is present in many vanadium oxide compounds with intermediate oxidation state between V^{5+} and V^{4+} . It is attributed to the stretching of short $V=O$ bonds that are also present in B phase VO_2 [33]. The broad vibrational band 534 cm^{-1} , attributed to the V–O–V octahedra bending modes [33]. Generally, the IR band of $V=O$ in crystalline V_2O_5 showed at 1015–1020 cm^{-1} . The band at 1015 cm^{-1} was assigned to the $V=O$ stretching vibration, while that at 825 cm^{-1} was attributable to the coupled vibration between $V=O$ and to V–O–V [34,35]. The band at 520 cm^{-1} was assigned to the V–O–V symmetric stretch of V_2O_5 [36,37].

Nano-micro rodlike structured were obtained from the sample (without ACA) calcined at 400 °C for 4 h (Fig. 8(a)). Fig. 8(b) shows a representative SEM image of the V_2O_5 (with ACA condition) calcined at 400 °C for

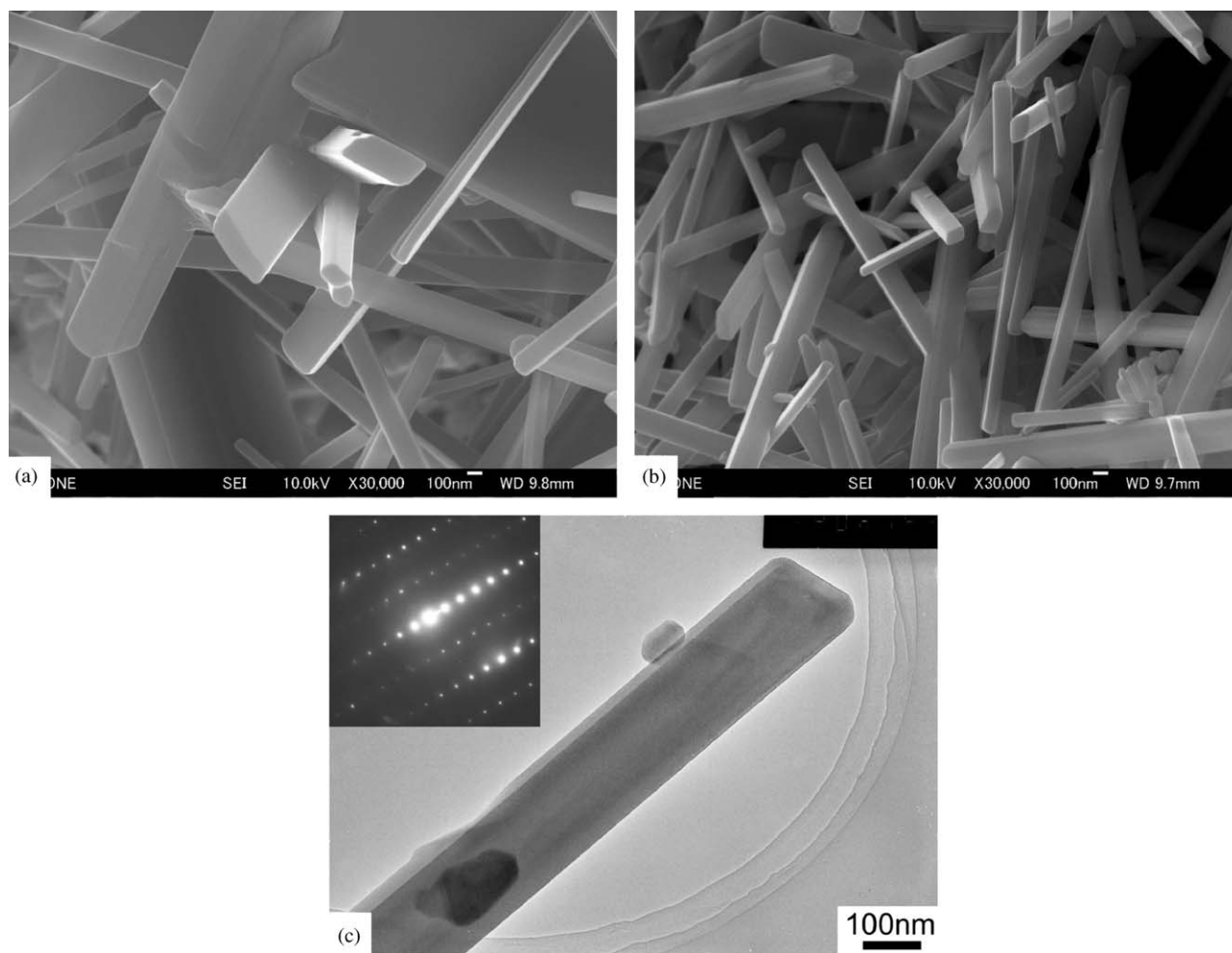


Fig. 8. SEM (a) image of V_2O_5 nano-micro rods (without ACA condition) calcined at 400 °C for 4 h. SEM (b), TEM (c), SAED (inset of c) images of V_2O_5 nanorods (with ACA condition) calcined at 400 °C for 4 h.

Table 1

BET surface area of the as-synthesized VO₂, V₂O₅ calcined at 400 °C for 4h, V₂O₅ by sol–gel method, and commercial vanadium oxides

Oxides	BET surface area (m ² /g)
VO ₂ (as-synthesized)	40
VO ₂ (Aldrich)	1
V ₂ O ₅ (calcined at 400 °C, 4h)	35
V ₂ O ₅ (by sol–gel)	10
V ₂ O ₅ (Aldrich)	6

4h. The image indicates more uniform size (compared with Fig. 8(a)) rodlike structured with the widths about 100–500 nm, the thickness of 100–300 nm, and the length of 1–10 μm. The single crystalline V₂O₅ nanorods were observed (Fig. 8(c)). The BET surface area of the as-synthesized and calcined sample were about 40 and 35 m²/g, respectively (Table 1). Owing to their uniform nanostructured, high crystallinity, and high surface area, distinguished electrochemical properties could be expected from these vanadium oxides nanorods.

Tungsten oxides and magnesium oxides nanowires were also synthesized using the same route of vanadium oxides nanorods by changing alkoxide precursors. Further study is in progress.

4. Conclusions

In summary, the operation of this synthesis method is a simple hydrothermal method and all the reactions of the synthetic process are carried out in aqueous solution under mild conditions. The hydrothermal process using surfactant enabled to fabricate vanadium oxides nanorods with controlled finer diameter. The rodlike structure in this study had high crystallinity with the widths 50–500 nm, thickness of 15–300 nm, the lengths of 1–10 μm, and high surface area (35–40 m²/g). These materials are promising for chemical and energy-related applications such as catalysts, and electrochemical device. Moreover, this method should be able to be extended to the synthesis of 1-D nanostructured metal oxides.

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