Front. Chem. China (2006) 3: 260–263
DOI 10.1007/s11458-006-0039-4

RESEARCH ARTICLE

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Synthesis, characterization and hydrogen storage capacity of MS_2 (M = Mo, Ti) nanotubes

Abstract The structure, morphology and hydrogen- storage capacity of MS_2 (M = Mo, Ti) nanotubes prepared by different experimental methods were studied. It was found that the MoS_2 nanotubes treated by KOH displayed the gaseous storage capacity of 1.2 wt% hydrogen (under the hydrogen pressure of 3 MPa and 25℃) and the electrochemical discharge capacity of 262 mAh/g (at the discharge current density of 50 mA/g and 25℃) that corresponds to about 1.0 wt % hydrogen. In comparison, TiS_2 nanotubes can store 2.5 wt% hydrogen under the hydrogen pressure of 4 MPa and 25℃. The results show that MS_2 compound nanotubes are promising materials for hydrogen storage.

Keywords hydrogen storage, MoS_2, nanotubes, TiS_2

1 Introduction

The emission of fossil fuels and increasing environment pollution have resulted in increased attention to the development and utilization of clean energy. Hydrogen is considered one of the most promising energy carriers in satisfying the increasing demand for clean energy [1]. However, a safe and high-efficient hydrogen storage must be obtained. For gaseous hydrogen fuel tanks to be used in vehicles, the targets of US Department of Energy (DOE) is to achieve more than 6.5% gravimetric and 62 kg H_2/m^3 volumetric densities of hydrogen. The available capacity of hydrogen storage system in vehicles should be more than 3.1 kg (which is as much as the amount of fuel used by small cars to run 500 km) [2]. Hydrogen can be stored using physical methods such as physical condensation and adsorption, or chemical metallic/complex hydrides [3]. Until now, no method for hydrogen storage, except liquid hydrogen stored in cryogenic tanks, has been found to meet all the requirements mentioned above. Therefore, it is very crucial to develop advanced materials for high-efficient hydrogen storage.

Like graphite, transition-metal disulfide such MoS_2 and TiS_2 have a planar structure, and their nanotube structure can be obtained in some special cases [4]. On the base of our previous work [5–9], we combined the favorable thermodynamics presented by the hydrogen storage alloy and the appropriate adsorption/desorption kinetics of nanostructu-red materials (such as carbon nanotubes [10]) to investigate the hydrogen storage capacity of MoS_2 and TiS_2 nanotubes in this paper.

Translated from *Acta Scientiarum Naturalium Universitatis Nankaiensis*, 2005, 38(4) (in Chinese)

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2 Experimental

2.1 Preparation of MoS_2 and TiS_2 nanotubes

The mixture of 5 g $(NH_4)_2MoS_4$ and 25 g stainless steel balls of 6 mm diameter was sealed in a stainless steel vial. The container was vacuumed and then filled with Ar through a connection vale, and repeated several times to completely eliminate the atmosphere. The ball milling was carried out in a QM-1SP2 apparatus at a speed of 500 rpm for 2 h.

An Al_2O_3 substrate, on which the ball-milled $(NH_4)_2MoS_4$ powder was homogeneously loaded, was put in a furnace as described [11]. High-purity hydrogen gas and a little of C_4H_3S vapor were introduced into the furnace; the volume ratio of hydrogen to C_4H_4S and the total gas flow rate can be adjusted in the experiments. The off-gases were diverted through a three-way valve to a sample loop for gas chromatograph analysis or a dimethylformamide (DMF) solvent and an aqueous solution of $ZnSO_4$ with the concentration of 1 mol/L to absorb the C_4H_4S vapor and eliminate the side products of H_2S and NH_3, respectively. The gas chromatograph showed that C_4H_4S took the role of catalyst. Due to

large experimental improvements, the optimized conditions were finalized at a volume ratio of H_2/C_4H_4S = 19:1, a total gas flow rate of 120 mL/min, a heating temperature of 300℃, and a total heating time of 30 min.

For the preparation of TiS_2 nanotubes, the mixture of Ti and S powder in an atomic Ti/S ratio of 1:2 transported by iodine vapor as the transport agent was run typically at 750℃ in a quartz tube at a pressure of 10^{-2} Pa. After reaction for 72 h, the dark brown product was obtained and was subsequently washed with absolute ethanol, dried in a vacuum at 100℃ for 2 h. It was found that iodine vapor played the role of transport media and the optimized concentration was 2–3 mg/cm^3. The preparation of MS_2 (M = Mo, Ti) nanotubes can be described by Eq. 1 and 2, respectively.

$$(NH_4)_2MoS_4 + H_2 \xrightarrow[300]{C_4H_4S} MoS_2 + 2NH_3 + 2H_2S \quad (1)$$

$$Ti + 2S \xrightarrow[750]{I_2} TiS_2 \quad (2)$$

2.2 Characterization of the above-synthesized samples

The composition, structure and morphology of the above-prepared samples were characterized by inductively coupled plasma emission spectroscopy (ICP, Thermo Jarrell Ash ICP 9000 (N + M)), powder X-ray diffraction (XRD Rigaku D/max-2500 X-ray generator; Cu Kα radiation, λ = 0.15406 nm), scanning electron microscopy (SEM, JEOL JSM-5600 and JEOL JSM-6700L Field Emission), transmission electron microscopy (TEM) and HRTEM (Philips Tecnai F20, 200 kV)

2.3 Gaseous storage in MS_2 nanotubes

The pressure-composition-temperature (PCT) measurements of polycrystalline MoS_2, untreated and KOH-treated MoS_2 nanotubes, and the above-prepared TiS_2 nanotubes were determined using an automated Sieverts-type apparatus (Advanced Materials Corporation) at the given temperatures. The volume in the hydriding/dehydriding process was carefully calibrated before the actual measurement. Ultra-high purity hydrogen (99.999 %) was used. Temperature was accurately controlled.

2.4 Electrochemical storage in MoS_2 nanotubes

The above-synthesized MoS_2 nanotubes were treated in the aqueous solution of KOH at 50℃ for 1 h. The treated MoS_2 nanotubes were washed with distilled water several times, and then dried in a vacuum at 80℃ for 1 h. The MoS_2 nanotube electrode was prepared by compressing the mixture of treated MoS_2 nanotubes, nickel powder and polytetrafluoroethylene (PTFE) in a suitable ratio. The MoS_2 nanoutbe electrode was tested in one open cell by using a sintered $Ni(OH)_2$/NiOOH counter electrode and an Hg/HgO reference electrode in 5 mol/L KOH solution. Electrode properties were measured using a Solartron SI 1260 Potentionstat Anslyzer with 1287 Interface and LAND (2001 CT-10mA) charge-discharge unit at controlled temperatures. The discharge capacity of the MoS_2 nanotube electrode was based on the amount of active material, excluding the weight of additives.

3 Results and Discussion

3.1 Characterization of MoS_2 and TiS_2 nanotubes

Figure 1 shows the XRD patterns of the ball milled $(NH_4)_2MoS_4$ before and after thermal reaction. The peak at 2θ of 17.2° for the sample before thermal reaction reveals that the phase has an orthorhombic structure (JCPDS-ICDD, No. 48–1662). The peak broadening is due to the very fine grain size and defects produced during the high-energy ball milling process. However, the characteristic peaks of $(NH_4)_2MoS_4$ for the sample after thermal treatment (Fig. 1b) disappeared, and new peaks appeared with relatively strong intensities. All of the peaks in Fig. 1b can be indexed to the hexagonal structure with lattice constants of $a = b$ = 0.316 7 nm, c = 1.2367 nm, which are in agreement with the values of polycrystalline MoS_2 (ICDD-JCPDS Card No. 39-1492).

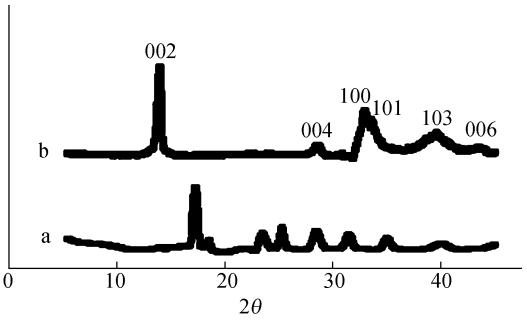

Fig. 1 XRD patterns of ball milled $(NH_4)_2MoS_4$ before (a) and after (b) thermal reaction

Figure 2 shows SEM image of the above-synthesized MoS_2 nanotubes obtained through thermal reaction, displaying that the MoS_2 nanotubes have a wire-like nanostructure, and are 3–5 μm in length and 25–50 nm in diameter. Figure 3 is the HRTEM image of the MoS_2 nanotubes, further demonstrating that the above-synthesized MoS_2 consists of nanotubes with regularly arranged layers. The inner diameter of an individual hollow tube is about 10 nm and the outer diameter is about 20 nm. The result of energy dispersive X-ray spectroscopy (EDS) analysis shows the presence of Mo and S with the atomic ratio of 1:2. Therefore, the above-synthesized product is MoS_2 nanotubes with high purity. The TEM observation suggests that the KOH treatment of MoS_2 nanotubes produce more defects, which can increase the specific surface areas of the product.

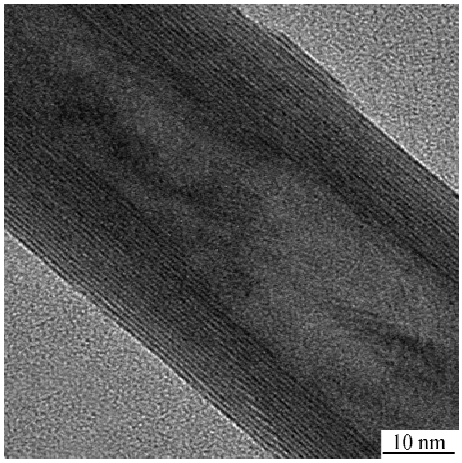

Fig. 2 SEM image of MoS_2 nanotubes

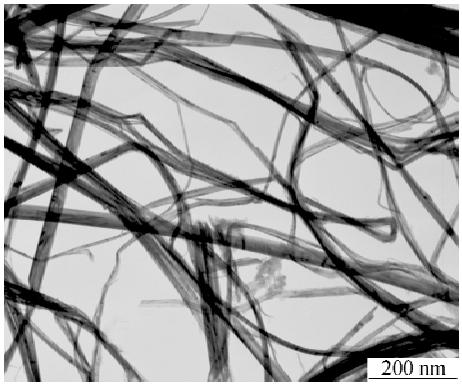

Fig. 3 HRTEM image of MoS_2 nanotube

TiS_2 nanotubes have also been prepared. The XRD analysis demonstrate that the product had a hexagonal structure with lattice constants of $a = b = 0.340\ 5$ nm, and $c = 0.569\ 2$ nm in accordance with the values of TiS_2 (JCPDS-ICDD No. 15–0853). Note that there were no diffraction peaks for other impurities, indicating the high purity of the as-synthesized TiS_2. The SEM image of TiS_2 displays a large quantity of wirelike nanostructure, and the TEM and HRTEM investigation indicate that the TiS_2 nanowires with open-ended tips have a hollow tubelike nanostructure. The ICP measurement reveals that the products synthesized by chemical transport reaction consist of Ti and S with the mole ratio of 1:2, indicating that the molecular formula of the as-synthesized product is TiS_2.

3.2 Gaseous hydrogen storage in MoS_2 and TiS_2 nanotubes

With the increase in hydrogen pressure, the quantity of hydrogen absorbed in MoS_2 and TiS_2 nanotubes gradually increased. The hydrogen content in MoS_2 nanotubes increased significantly below 1 MPa, and this process was completed below 3 MPa. The ultimate hydrogen concentration in TiS_2 nanotube is achieved below 4 MPa, which corresponds to the absorption capacity of 2.8 hydrogen atoms per TiS_2 molecule (2.5% in gravimetric density of hydrogen). An increase in temperature causes a decrease in hydrogen content. However, considerable amounts of hydrogen can be still stored reversibly in nanotubes. The adsorption/desor-ption process of the nanotubes can achieve equilibrium in short period, indicating the kinetic advantage of nanomaterials for gas adsorption/desorption. Table 1 illustrate the gaseous hydrogen storage capacity of MS_2 (M = Mo, Ti) nanotubes at 25℃.

This order indicates that more defects in MoS_2 nanotubes produced by KOH treatment cause higher specific surface areas and improved hydrogen adsorption behavior. Because Mo is a heavy metallic element, TiS_2 nanotubes are better to increase hydrogen storage density.

3.3 Electrochemical storage

Figure 4 shows the discharge curves of the MoS_2 nanotube electrodes at different current densities. An obvious discharge plateau was observed between –0.80 V and –0.86V (vs. Hg/HgO), revealing that large amount of hydrogen desorbed from the nanotubes. However, the discharge slopes, which are not as flat as those of conventional metal hydride electrodes, show the existence of different hydrogen adsorption-(absorption)/desorption sites. The maximum discharge capacity for MoS_2 nanotubes was 262 mAh/g at the current density of 50 mA/g at 25℃, corresponding to about 1.0 wt% absorbed hydrogen. A reversible adsorption-(absorption)/desorption capacity of 1.6 hydrogen atoms per MoS_2 molecule was achieved, according to Faraday's law. After testing 100 consecutive cycles of charging/discharging (100% DOD at 50 mA/g), the capacity of the nanotube electrode decreased by only about 5 %, showing a stable electrode property.

4 Conclusions

High-purity and open-ended MS_2 (M = Mo, Ti) nanotubes were synthesized by different methods. The electrochemical investigation indicated that the maximum electrochemical hydrogen storage capacity of MoS_2 nanotubes was 262 mAh/g at the current density of 50 mA/g at 25℃. The gaseous

Table 1 Hydrogen storage capacity of MS_2 nanotubes (M = Mo, Ti) at 25℃

Sample	Polycrystalline MoS_2	MoS_2 nanotube		TiS_2 nanotube
Hydrogen storage capacity/wt%	0.2 (3 MPa)	without KOH treatment	with KOH treatment	
		1.0 (3 MPa)	1.2 (3 MPa)	2.5 (4 MPa)

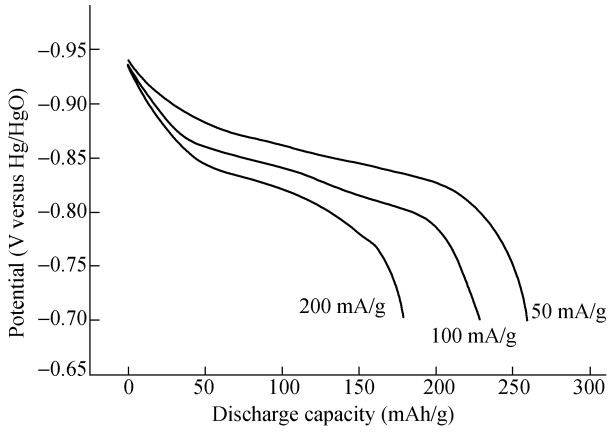

Fig. 4 The discharge curves of the electrode made by KOH-treated MoS_2 nanotubes

hydrogen storage capacity of 1.2 wt% was obtained for MoS_2 nanotubes at 3 MPa at 25℃. In comparison, the above-synthesized TiS_2 nanotubes can store 2.5 wt% hydrogen at 4 MPa at 25℃. The MoS_2 and TiS_2 nanotubes show favorable adsorption(absorption)/desorption capacities and kinetics for hydrogen storage. However, the density of higher hydrogen storage should be further improved.

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