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Sensor properties of vanadium oxide nanotubes

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Vanadium oxide nanotubes synthesised with hexadecylamine-1 as a structure-directing template were tested as gas sensitive elements for oxygen, nitrogen oxide, triethylamine (TEA) and dimethylmethylphosphonate (DMMP).

Vanadium oxides are widely used as catalysts,[1] electrochromic and thermochromic devices,[2] thin films of vanadia are tested in ethanol sensors.[3] New one-dimensional (1D) nanomaterials attract great attention in view of their future applications.[4] Unfortunately, one-dimensional structures in the V–O system are much less investigated compared to other systems such as carbon nanotubes despite of their easy preparation in the forms of vanadium oxide nanotubes,[5] nanobelts[6] or nanowires[7]. Most of these materials were examined as cathode materials although it is also of great interest to find out if they can serve as active elements in other practically important devices.

Particularly, the elaboration of new promising materials for chemical sensors is highly demanded because of a growing amount of various risks of dangerous gas escape, water pollution *etc*. Polycrystalline V_2O_5, vanadium bronzes and $V_2O_5 \cdot nH_2O$ xerogels are considered as prominent sensor materials for the quantitative detection of atmospheric humidity, ethanol vapour,[3] nitrogen dioxide, oxygen,[1] amines[8] *etc*. Recently, the nanobelts of vanadium oxide have been reported to be a promising and stable material for ethanol sensors.[6,9]

Vanadium oxide nanotubes can be prepared in a high yield[10] and with a unique structure of multilayer scrolls[11] having the interlayer distance easily controlled by a proper choice of structure-directing templates involved in a hydrothermal process.[4,12,13] This technique was used in this work to treat orthorhombic polycrystalline V_2O_5 as an inorganic precursor and hexadecylamine-1 (HDA) with a chain length of 2.15 nm as a template to prepare vanadia nanotubes (VNTs) with interlayer distances of 3.2–4.3 nm.[11,14] Both vanadia and HDA were stirred for two days under ambient conditions to form a layered precursor. The hydrothermal treatment of the precursor was performed at 180 °C for 48 h. The product was repeatedly washed with distilled water and ethanol and then dried at 60 °C in air.

Thermal analysis of the product was performed using a Pyris Diamond TG-DTA thermoanalyzer (Perkin–Elmer). Standard platinum crucibles and a heating rate of 5 K min^{-1} were used. XRD was measured by a Rigaku D/MAX 2500 diffractometer (Japan) with a rotating copper anode (CuKα) in a 2θ range of 3–70° with a step of 0.01°. The morphology of VNTs was investigated on a Leo Supra 50VP scanning electron microscope (Germany) and a Hitachi-8100 transmission electron microscope (Japan).

During the hydrothermal treatment, as-formed nanotubes are stuck together in bundles (Figure 1), making it not so easy to separate the individual nanotubes. Prior to the measurements, the VNTs powder (about 20 mg) was grinded in α-terpineol

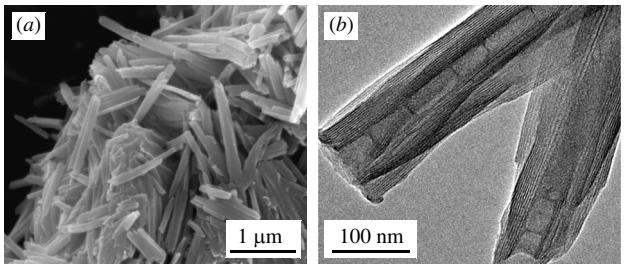

Figure 1 Morphology of VNTs: (*a*) a general view of as-prepared bunches of VNTs (SEM micrograph), (*b*) an internal structure of the VNTs after annealing at 200 °C for 6 h (TEM micrograph).

($C_{10}H_{17}OH$) as a binder. Then, the paste was screen-printed onto a special chip with four platinum contacts located on a single-crystalline quartz substrate. Terpineol was burnt out by calcination at 200 °C. We studied the gas effect on electrical resistance in potentiostatic regime in a dynamic flow system with dry air as a carrier gas. The total flow rate in all measurements was 100 ml min^{-1}.

Thermal stability studies of nanotubes demonstrate that there is a strong exothermic peak and a high decrease of the weight at 250 °C limiting the working range of such a sensor. The stability of the nanotube structure was also confirmed by XRD and TEM. The preserved layered structure of individual nanotubes after heating and annealing for 6 h at 200 °C is shown in Figure 1(*b*). The inner space in the central parts of nanotubes is hollow and almost free of a surfactant; the interlayer distance in nanotubes was 3.26 nm. Annealing also forms some freaks [Figure 1(*b*)]. The XRD of the initial nanotubes and the nanotubes annealed at 200 °C look quite similar (Figure 2) since the spectra demonstrate a structure with relatively large interlayer distances. A more detailed discussion of TG–DTA data was published elsewhere.[14]

Table 1 The values of sensitivity *S* of VNTs for given gas mixtures at different temperatures.

Test gas	Concentration	Temperature/°C	$S = R_{max}/R_{min}$
TEA	10 ppm	125	1.005
TEA	10 ppm	200	too low resistance
TEA	0.6 ppm	200	too low resistance
DMMP	0.6 ppm	200	step-by-step growth
O_2	0.5–20%	150–180	step-by-step growth
NO_2	0.8 ppm	100	1.005
NO_2	0.8 ppm	175	1.03
NO_2	0.8 ppm	200	1.01

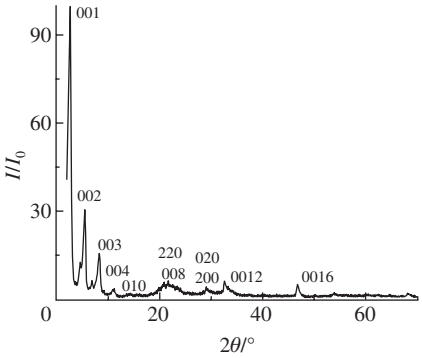

Figure 2 XRD of as-prepared VNTs.

All the measured gas-sensing characteristics of the nanotubes are summarised in Table 1, in which the sensitivity S is defined as $S = R_{max}/R_{min}$, where R_{max} and R_{min} are the sample resistances with or without an analysing gas in artificially prepared mixtures. We measured the electric transport through the samples at 200, 175, 150, 125 and 100 °C starting from the highest temperature. Most of the gases tested show a better sensitivity at temperatures lower than 200 °C because conductivity drastically increases with temperature. In most cases, VNTs exhibit a quite reproducible behaviour, *i.e.,* their resistance reaches initial values as soon as a test gas is shut off (see Figure 3).

The highest sensitivity of the nanotubes was observed in the case of TEA (Table 1). When interacting with amine molecules at 200 °C, the nanotubes increase their conductivity so significantly that the sensor signal cannot be routinely detected (Table 1). At 125 °C, the sensitivity of nanotubes was about 1.005. At a lower concentration of TEA (0.6 ppm), similar results were observed. This interaction of VO_x nanotubes with TEA molecules could be the result of a redox process between V(V) and TEA. When the oxidation of long-chain HDA molecules within the structure of nanotubes occurs only at about 250 °C the oxidation of TEA by the nanotubes is possible even at 150 °C.

To the contrary, nitrogen dioxide could be an oxidizing agent for mixed-valent VO_x in nanotubes. The interaction of NO_2 molecules with the nanotubes has demonstrated a detectable sensor signal at 100–200 °C. The maximum sensitivity was observed at about 175 °C.

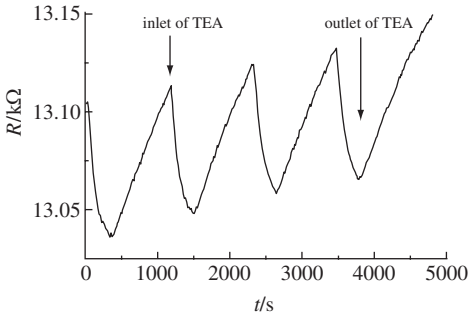

Figure 3 Test of sensor properties of VNTs at 125 °C observed for TEA.

The sensitivity of nanotubes to oxygen on heating was examined in the concentration range 0.5–20% O_2. At about 150–180 °C, molecular oxygen oxidises the nanotubes and thus slowly increases their resistance without a suitable sensor signal.

In summary, vanadium oxide nanotubes demonstrate a semiconductor character of conductivity; additionally, the growth of the material conductivity with temperature can be caused by an increase in the V^{IV} content in the structure as a result of redox reactions of V^{V}. The electric contact between nanotubes is also realised through tunneling between outer walls that are adjoined or fused with one another. All of these could be possible reasons of 'chemical sensitivity' of the nanotubes. Thus, the applications of VNTs as a novel material for gas sensors are promising. In particular, it was observed that the nanotubes demonstrate a detectable sensor signal with respect to TEA even at 125 °C, while this material is not sensitive to the rippling of concentrations of oxygen and DMMP.

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