

PREPARATION AND CATALYTIC TEST OF VANADIUM OXIDE NANOWIRE-CARBON NANOTUBE COMPOSITES

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1-D nano-sized fibrous and tubular inorganic structures have attracted special attention upon their outstanding structural flexibility and unique chemical and physical properties. Vanadium oxide wires are of specially interest for catalytic sciences due to their intrinsic highly variable valency and excellent redox properties.¹ Vanadium oxides and related compounds are frequently employed as the catalysts for partial oxidation or dehydrogenation of alkanes.^{2,3} Most of these reactions are highly exothermic. The reaction-released heat hoards on the catalyst surfaces and thus declines the catalytic activity or selectivity because the thermal conductivity of the active catalysts and/or the normally employed supports are very low. Such a problem is possibly solved by employing special supports with high thermal conductivity², which act as a heat-pump to extract the heat from the catalyst surface and reactor. Carbon nanotubes (CNTs) have an excellent thermal conductivity, high surface area, and high thermal and chemical stability's. Furthermore, it has been well known that carbon material themselves, including nanofibres,⁴ are also active and selective for some catalytic oxidation reactions. Therefore, combining vanadium oxides with CNTs is expected to produce a novel catalytic material and to improve the catalytic behavior. In this work, we report a novel approach for the preparation and characterization of vanadium oxide nanowires (VONWs) and CNT composites.

Multi-walled tubes with diameters of 10-50 nm were obtained by a detonation of mixed picric acid, paraffin, and cobalt acetate⁵. Before using, they were oxidised with 6 M HNO₃ at refluxing temperature for 12 h to modify the tube surfaces with oxygen-containing groups. To synthesize the VONW-CNT composites, the CNTs are pretreated by nitric acid solution to partially remove the impurities (cobalt and amorphous carbon particles) and to modify oxygen-containing groups on the tube surface. 100 ml solution of NH₄VO₃ (0.04-0.08 M) containing 100 mg oxidized CNTs was refluxed for 5 h with magnetic stirring. After the refluxing, the suspension was filtrated, washed with deionized water and ethanol, and dried at 110 °C overnight.

The hydrolysis of NH₄VO₃ can effectively produce vanadic acid or VO_x at refluxing temperature but leads to heavy aggregation – formation of irregular micrometer particles, rendering the control of size and shape difficult. When surface-modified CNTs are introduced into an aqueous NH₄VO₃ solution, the hydrolysis leaves behind well-grown VONWs, with lengths of up to 20 µm and widths of 5-15 nm (Figure 1a). The VONWs are often separated from the CNTs and are normally organized as bundles. Previously reported CNT-assisted production of 1-D V₂O₅ nanostructures applied molten V₂O₅ or HVO₃ gel on tube surfaces and/or filled internal cavities, such that CNTs act as geometric templates.⁶ In the present approach towards VO_x nanowires, however, CNTs serve as inducers by partially providing their curved surfaces (Figure 1b) for inducing the nucleation of the VO_x nanostructures. This is fully

confirmed by the TEM observations of wire morphologies and wire-tube existing states.

The VO_x nanowires exhibit an average O/V atomic ratio of 3.8 as revealed by EDX analyses. X-ray powder diffraction confirms the mixed composition of V₂O₅·H₂O and 6VO₂·5H₂O. The crystals are well-structured and exhibit the (001) planes normal to wire axis (HRTEM), suggesting that the nanowires grow along [010] direction. Thermal stability of vanadium oxide nanostructures is crucial for their practical applications in catalysis. Unlike the tubular nanostructures obtained by an organic amine-directed hydrothermal route, decomposing above 250 °C,⁷ the present nanowires are rather stable in morphology at temperatures as high as 400 °C in air, although the wire surfaces become rough and most of the water molecules in the crystals are lost after the heating treatments. The first catalytic test for n-butane partial oxidation shows that the composite is active towards formation of maleic anhydride at a temperature as low as 200°C. Detailed results will be presented at the conference.

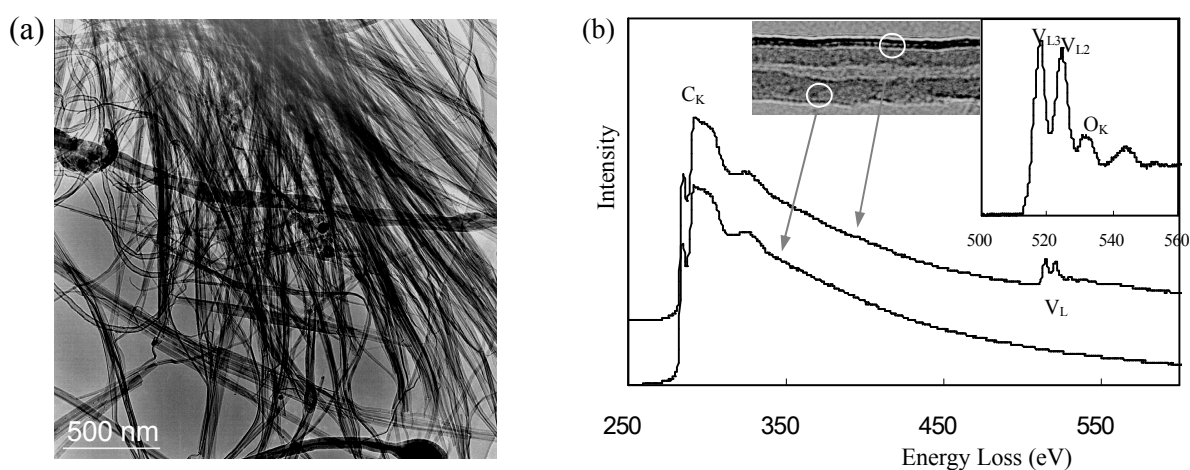


Figure 1. (a) TEM image of the materials obtained from NH₄VO₃ hydrolysis in the presence of CNTs. (b) EELS obtained on two different sides of a carbon tube (left inset). One side is coated with a thin film of vanadium oxide, while the other side shows no vanadium. The right inset is the magnification of the vanadium oxide spectrum.

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