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Anatase nanotubes as support for platinum nanocrystals

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Abstract

Anatase nanotubes were successfully produced via the sol–gel process involving organic titanium precursors and multi-walled carbon nanotubes as template. Controlled heat treatments were carried out in order to remove any solvents and to crystallise the initial amorphous titania coating into anatase. In order to use these structures for catalyst support, platinum particles were formed by the impregnation with hexachloroplatinic acid and subsequent calcination and reduction to obtain a final loading of 4 wt% platinum. This impregnation step was carried out either with the carbon nanotube former still present with subsequent heat treatment to remove the carbonaceous template (sample A) or with the carbon nanotube former already removed (sample B). The materials were characterised by X-ray diffraction, scanning electron microscopy and transmission electron microscopy.

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1. Introduction

Considering the enormous importance of TiO_2 in the fields of photo-catalysis [1–4], solar cells [5], environmental catalysis [6,7] and gas sensing [8–10], the fabrication of this material in a nanoscale anisotropic morphology is of great interest. Nanotubes and nanofibrils have a particular advantage in the way they enable three-dimensional, mechanically coherent architectures, which provide ready gas access to a high surface area. For instance, Grimes showed that the use of titania nanotubes (TiO_2-NTs) coated with palladium particles leads to a 1000 fold higher sensitivity for sensing small hydrogen concentrations in the atmosphere, compared to a particle-based substrate [11]. Additionally, TiO_2-NT-based sensors can be operated at room temperature and thus exhibit a longer lifetime [12]. Another group studied the possible application of TiO_2-NTs in dye-sensitised solar cells and documented a significantly higher photolytic efficiency [13]. In all these studies a significant difference of the physical and chemical properties between TiO_2-NTs and TiO_2 particles was measured.

In view of these works, the use of TiO_2 nanotubes as supports for metal nanoparticles seems to be promising for both photo- and environmental catalytic applications. For instance, Lin et al. [14] used $H_2Ti_3O_7$ nanotubes with 1% platinum to study the photocatalytic dehydrogenation of ethanol to hydrogen, their activity was strongly influenced by the preparation procedure of the titania nanotubes . Recently, Sato et al. [15] studied the catalytic behaviour of Pt/TiO_2-NTs for the water gas shift as well as the CO hydrogenation reaction. The observed catalytic activities were higher by at least a factor of 3 compared to conventional impregnated Pt/TiO_2 catalysts. Although their results are promising and suggest an enhancement in catalytic properties upon applying nanotubular TiO_2 as catalyst support, they compared two completely different materials: their nanotubular catalyst was found to exhibit a predominantly rutile structure with small platinum particles ($d\sim0.3$–0.5 nm) being incorporated inside the tubes' wall. By contrast, the conventional catalyst support was of pure anatase and platinum particles were deposited on the surface via wet impregnation. Furthermore, the amount of platinum inside the tubes' wall was calculated to be 30 wt%

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with an average dispersion of 0.09, whereas the conventional catalyst was prepared with 3 wt% platinum with a dispersion of 0.16, both dispersions being measured by hydrogen adsorption. Despite this inconsistency, it is of much interest to investigate the differences between anatase and rutile as catalyst supports in both nanotubular and nanoparticular morphologies with controlled and comparable specific surface areas, platinum content and dispersion.

The first titania nanotubes were produced by Kasuga in 1998 via hydrothermal treatment of TiO_2 particles in concentrated NaOH solution at temperatures above 110 °C [16]. Following his discovery, extensive studies have been carried out to understand the growth mechanism of titania nanotubes whose predominant structure was found to be $H_2Ti_3O_7$ [17]. Anatase nanotubes have been produced via anodic oxidation of titanium sheets [18] as well as via sol–gel coating using porous alumina templates [19]. However, the production of nanostructured rutile materials with considerably high specific surface areas that are also stable at elevated temperatures, such as needed for catalyst activation, had been a challenge until recently. So far, rutile was typically produced via phase transformation of anatase at high temperature, during which the crystals grew and thus the surface area decreased significantly [20]. Rutile crystals were also produced directly by homogenous precipitation [21] exhibiting a very high surface area, which however decreased rapidly as soon as the temperature was increased. Hitherto, all attempts to phase transform anatase nanotubes into rutile nanotubes were not successful. Recently, we reported the production of nanotubes consisting of pure rutile involving the sol–gel route and sacrificial carbon nanotube templates, with subsequent heat treatment being used to covert the templated anatase to rutile, while supporting the structure during the reconstructive phase transformation [22,23]. The carbon templates can be subsequently burnt out to leave pure rutile nanotubes. Alternatively, anatase nanotubes are prepared in a similar way [24]. Both materials show exceedingly high surface areas up to approximately 160 and 120 m^2/g for anatase and rutile nanotubes, respectively.

Therefore, in this work we apply these novel materials as supports for platinum catalysts prepared via a standard wet impregnation process. Characterisation was performed by electron microscopy methods (SEM, TEM) as well as by X-ray diffraction (XRD), and combined thermal analysis (TGA/DSC).

2. Experimental

Template: Multi-walled carbon nanotubes (MWCNT) were used as templates and were produced in a modified CVD process in a tube furnace reactor using ferrocene as catalyst precursor and toluene as the feedstock [25]. The average outer diameter of the nanotubes was 70 nm and the length was between 20 and 30 μm (Fig. 1(a)).

Titania coating: The carbon nanotubes were coated by a sol–gel template method, followed by a hydrothermal treatment and calcinations in either air or in flowing nitrogen up to temperatures of 600 °C [22]. In a typical experiment, the carbon nanotubes were dispersed in ethanol with the aid of ultrasonication for 10 min. Benzyl alcohol (BA) and water were then added and the solution stirred at 0 °C. As titanium precursors, tetrabutyl-orthotitanate (TBOT, $Ti(n\text{-}Bu)_4$) or titanium isopropoxide (TI, $Ti(t\text{-}OPr)_4$) were dissolved in ethanol and slowly dropped into the CNT suspension, so that the final molar ratio was 1:3:6:30 (TBOT:BA:H_2O:ethanol). During this process the titanium precursor hydrolyses with water to form hydroxyl groups that will condense in the further process to build up a gel-type Ti–O–Ti network. After 1 h of stirring, the precipitate was filtered, washed in ethanol and dried in air at room temperature followed by calcination in air at temperatures up to 400 °C (Fig. 1(b)). A subsequent heat treatment in air at 550 °C was needed to oxidatively remove the carbonaceous template (Fig. 1(c)).

Catalyst deposition: The TiO_2 nanotubes as well as the TiO_2 coated CNT were impregnated with platinum designed to obtain a final content of 4% [26]: a solution of the desired amount of hexachloroplatinic acid (H_2PtCl_6) in deionised water was slowly dropped into a suspension of anatase nanotubes (with and without CNT) in water, which was kept stirring at room temperature over night to remove all solvents. The so-prepared catalysts were then calcined in flowing oxygen at 400 °C (ramp 5 °C/min) and subsequently activated in flowing hydrogen. Each treatment was performed for 2 h.

The morphology was studied by a high resolution scanning electron microscopy (JEOL 6340F FEG-SEM). High-resolution transmission electron microscopy (HRTEM) was applied to examine the microstructure of

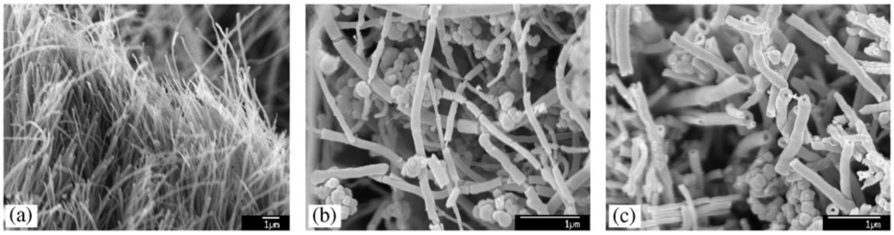

Fig. 1. SEM images taken from (a) the carbon nanotube template, (b) carbon nanotubes coated with anatase after a heat treatment at 400 °C, and (c) anatase nanotubes after removing the carbonaceous template at 550 °C.