Formation of nickel oxide nanostructures on TiO$_2$.

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Abstract: A new method to prepare catalytic NiO templates for growing carbon nanotubes is described. The method utilizes sol-gel chemical reactions in formation of NiO containing nanostructures on TiO$_2$ surfaces. The structures are studied using X-ray photoelectron spectroscopy and atomic force microscopy methods.

1. Introduction

Since discovery of carbon nanotubes (CNT), different preparation techniques of CNT have been developed and studied by many investigators (see e.g. [1] and references therein). Currently, both randomly oriented and aligned CNT can be produced on laboratory as well as mass-production scales. Also, some characteristic properties of CNT like diameter and length can be varied by tuning the process conditions. Still there are numerous problems related to quality (uniformity), cost-effectiveness, and applicability issues in CNT production that seriously hinder mass-scale application of these unique structures.

Majority of production methods utilize metallic nanoparticles/structures as catalysts for growing CNT. For instance, in 2002, Tu et al. demonstrated possibility to grow aligned CNT using Ni nanoparticles as process catalysts [2]. Recently, Huang et al. showed that also NiO$_x$, templates prepared by AFM (Atomic Force Microscopy) nano-patterning technique are well-suited catalysts for selective growth of carbon nanotubes [3]. However, AFM nano-patterning technique is very elaborate, inefficient and expensive method for making such catalytic structures and therefore search for additional methods is appreciated.

In this work we present an alternative approach for preparation NiO nanostructures that can be used as catalysts for growing CNT's. We investigated the formation of NiO nanostructures during sol-gel process that is relatively simple, cost-effective and readily applicable method for preparation several oxide materials and different structures (see e.g. [4] and references therein). Our approach harnesses intrinsic self-assembling of precursor materials, and in contrast to above-mentioned method by Huang is therefore applicable over unlimited surface area and also in cases of complicated structures.
2. Preparation of samples

Nickel doped thin films were prepared by sol-gel method using commercially available titanium (IV) butoxide (Ti(O(CH$_3$)$_3$)$_4$) (Alfa Aesar, purity 99 %) and nickel (II) nitrate hexahydrate (dopant, Alfa Aesar, purity 99.9985 %) as the starting materials. Synthesis and doping procedure were similar as in our previous work [5]. Since the synthesis procedure is sensitive to presence of water, the used solvents (alcohols and alkanes) were dried and distilled before use. Polymeric precursor materials were prepared by adding mixture of dopant, mono distilled water and solvent (butanole) into titanium butoxide and stirring the mixture vigorously. The partial polymerization of titanium (IV) butoxide was carried out by adding water using molar ratio $R = \frac{[\text{H}_2\text{O}]}{[\text{Ti(O(CH}_3)_3\text{CH}_3]_4]}=1.54$. The atomic ratio of Ti$^{4+}$ and Ni$^{2+}$ in precursor was 24 to 1. After polymerization reaction the solvent was removed in vacuum at 7 mm Hg. Evaporation procedures were carried out on the Büchi R-114 Rotavapor® installation equipped with two-stage membrane vacuum pump and electronic vacuum controller. For the film deposition 23,3 % polymeric precursor solution in hexane was prepared. Thin films were prepared by dropping (from height of 5 mm) the precursor solution droplet (3 mg) onto monodestilled water surface at 21°C. The precursor polymerized rapidly and a floating thin film was formed on water surface. The films were collected on mica substrate by dropping the water level until the substrat surfaced and captured the film.

Before heat treatment the obtained thin films were kept at room temperature in air for 24 hours (later called “aging”). To release the remaining organic solvents and to crystalline the material, the films were baked in an oven (in air) raising the temperature to 700°C within 4h and keeping at the temperature from 1 to 10 h.

3. Characterization of samples using XPS

The X-Ray Photoelectron Spectroscopy (XPS) is a powerful method for characterization chemical composition of a sample surface. The XPS measurements of the present work were carried out using Thermo XR3E2 twin anode X-ray source with Al anode (exciting photon energy 1486.6 eV, anode voltage 15 kV). Photoelectron energies were measured using Scienta SES-100 electron energy analyzer. The angle between incoming photon beam and the axis of the electron energy analyzer was 45° and the sample normal was parallel with the axis of the electron energy analyzer. SES-100 was calibrated using Au 4f photolines. Photon energy resolution of the X-ray source was about 0.8 eV (FWHM) and the resolution of the electron energy analyzer was about 0.3 eV.

Figure 1. demonstrates XPS spectra of an aged sample (i.e. without baking) and a baked sample. In the photoelectron spectrum of the former the photoelectron lines in the region of Ni 2p states are missing. However, the baked sample shows clear Ni 2p photolines. The drastic appearance of Ni lines is caused already by the shortest baking of the samples. The relative intensity of Ni lines gradually increases as the baking time is increased.
Observed photoelectron lines are not typical for metallic nickel, which spectrum demonstrates two separated peaks ($2p_{1/2}$ and $2p_{3/2}$) and weak broad structures on the higher binding energy side of both peaks [6]. Measured distance between $2p_{1/2}$ and $2p_{3/2}$ lines for metallic Ni is 17.25 eV [7].

![Photoelectron spectra of aged precursor film and Ni-doped TiO$_2$ sample (after thermal treatment for 10 hours at 700 °C).](image)

Fig. 1. Photoelectron spectra of aged precursor film and Ni-doped TiO$_2$ sample (after thermal treatment for 10 hours at 700 °C). Excitation photon energy was 1486.6 eV.

In our case the separation of maxima of $2p_{1/2}$ and $2p_{3/2}$ lines is 18.6 eV and beside to electron lines the strong shake-up satellite bands are as well observable. Such picture is typical for NiO samples [6, 8]. It is reasonable to conclude that in the case of our samples NiO dominates, but other Ni compounds, e.g. Ni$_2$O$_3$ may as well exist.

Using ratios of Ti 2p and Ni 2p XPS spectral bands’ areas, respective transmission coefficients and taking into account different excitation cross sections [9], it is possible to calculate rough estimates of relative surface concentrations of Ni and Ti. The highest concentration of Ni was observed in the case of 10 h baked samples when the ratio 1:8 was achieved.
4. Characterization of samples using AFM

Investigation of morphological properties of the samples’ surfaces was performed with a SMENA-B atomic force microscope (NT-MDT). Typically a semicontact mode was utilized that is known to result in optimal performance in the case of such samples.

Fig. 2 presents the surface morphological characterization results of the samples before and after the 10 h thermal treatment at 700°C. The heating modifies the surface in a way that is characteristic to many oxide surfaces and has been observed previously in numerous occasions. Appearance of well-distinguished grains with mean diameter of about 40 nm can already be seen after 1h heating (Fig. 3(a)). Qualitative inspection revealed that the size distribution remained quite narrow and constant over macroscopic surface area. Further heating for up to 10 h causes only slight topographic modification of the samples’ surfaces, namely a small increase of grain sizes (Fig 3.(b)).

The topographic imaging has no means to distinguish between different materials. However, a phase imaging (i.e. monitoring the phase lag of the cantilever oscillation relative to the drive signal simultaneously with the topography data) goes beyond simple topographical mapping detecting variations in composition, adhesion, friction, viscoelasticity, and numerous other properties. Detail analysis and comparison of the phase images (Fig. 4) support the result of the XPS measurements that concentration of the surface Ni is increased as the result of the heating. Some evidences also support the speculation that Ni is concentrated into tiny nanostructures as seen in the case Ag in Ref. [10]. We hope to clarify the situation by microscopic analysis of regions of preferable growth of CNTs in the future.
5. Conclusions

We have shown that sol-gel method can offer a cost-effective possibility for formation of catalytic NiO templates for growing CNTs. The main benefits of the method are very simple variation of catalytic material, and its applicability at macroscopic scales and in cases of complicated structures. Future investigations will focus at demonstration of actual growth of CNTs and optimization of the process parameters.

Fig. 3 (a) AFM topographic image of sample heated 1h at 700 °C. (b) AFM topographic image of sample heated 10 h at 700 °C.

Fig. 4 A typical AFM phase image of a sample heated for 10 h at 700 °C.
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