EXPERIMENTAL AND THEORETICAL ASPECTS OF CCVD SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOTUBES ON AZO SUBSTRATE

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Abstract

During catalytic chemical vapor deposition (CCVD), the synthesis parameters and the quality of the catalyst thin film both have to be precisely tuned to synthesize VACNTs in an efficient and reproducible way. In this work, CNT forests were grown on AZO (aluminum doped zinc oxide) glass substrate which was coated *via* dip coating method with few nanometers thick Al_2O_3 support layer and bimetallic iron-cobalt catalyst layer. The study of the effect of catalyst composition and synthesis parameters during CCVD growth has revealed the optimal conditions to synthetize CNT forests on AZO. The samples were analyzed *via* SEM, TEM and Raman spectroscopy to verify the structure and quality of the carbon deposition. Theoretical aspects have confirmed the role of the support layer for conducting substrates during CCVD synthesis; the transformation of the catalyst layer in the presence of hydrogen gas and the growing mechanism of CNTs.

Introduction

Carbon nanotubes (CNTs) have been a prominent part of nanotechnology research for more than three decades [1,2]. CNTs can play an essential role in solving the growing energy and environmental crises [3,4] A unique type of CNTs, vertically aligned CNTs (VACNTs), have the exceptional nanoscale properties (mechanical, surface area, electrical and thermal conductivity) of individual CNTs, combined with a hierarchical and anisotropic morphology, which provides great potential for a wide range of practical environmental applications, from water filtration to energy storage [4–8]. Catalytic Chemical Vapor Deposition (CCVD) is the preferred method for the mass production of CNTs because it is cost-effective and easy to set up, moreover it is the only suitable technique for the synthesis of VACNTs [9]. In comparison to the possibilities for the synthesis of VACNTs, there are various methods to fabricate thin catalyst layers (e.g. atomic layer deposition (ALD), physical vapor deposition (PVD), pulsed laser deposition (PLD), magnetron sputtering (MS), dip coating, etc. [10,11]), which are able to control the layer thickness and morphology but require rather expensive instruments. Dip coating can be an exception to the above-mentioned methods, as it requires less complicated instruments, scalable and cost-effective, and therefore is widely used for catalyst deposition.
Transparent conductive oxides (TCOs) are drawing more and more attention in various research due to the infrastructural evolution of renewable energy exploitation [12,13]. The best known TCOs are indium tin oxide (ITO), fluorine tin oxide (FTO) and aluminum doped zinc oxide (AZO). ITO has been extensively used for various TCO applications (opto-, microelectronic devices, photovoltaic devices, such as sensors, solar cells, LEDs, display panels etc.) due to its suitable properties[14,15]. However, the lack of the rare earth indium, the natural brittleness of ITO and its high production costs have limited the mass production of flexible and low-cost devices [12,16,17]. ITO and FTO glass substrates are the most used and well known among TCO substrates, but their applications are limited for VACNT growth due to their temperature

sensitive properties [13]. In the literature, the suitability of AZO-coated glass substrates for VACNT growth was not found. Few studies have focused on thermodynamic analysis of aligned carbon nanotubes. The growth rate of CNT forests is affected by various parameters: the growth rate can be limited by the synthesis temperature, the quality and concentration of the catalyst, the type of gas precursor, the surface reactions on the catalyst particle, the diffusion of carbon through the bulk phase of the catalyst particle or on the surface of the catalyst particle [18].

In this work, the growth of vertically aligned carbon nanotubes on AZO glass substrate is demonstrated with and without Al_2O_3 support layer and Fe-Co bimetallic catalyst layer arrangement, which have not been used in previous research. Beyond the experimental approach, our aim was to have better understanding of the behavior of the support (alumina) and the catalyst layer under the applied reaction conditions.

Experimental

A simple and cost-effective thin layer deposition technique, dip coating method was used, firstly to build the support oxide layer with 0,11 mol/dm^3 absolute ethanol solution of aluminum nitrate and then to build bimetallic iron-cobalt catalyst layer at different molar ratios (0:1, 1:3, 2:3, 1:1, 3:2, 3:1, 1:0) with 0,11 mol/dm^3 mixture of absolute ethanol solution of cobalt(II) nitrate hexahydrate and iron(III) nitrate nonahydrate. Precursor solutions were freshly prepared to avoid undesirable components formation and degradation. The substrates with support and catalyst layers were annealed in a static oven at 400 °C for 1 h to stabilize the nitrate-based precursor layers on the surface.

The CCVD synthesis was performed in a horizontal quartz tube reactor (diameter 20 mm, length 80 mm) at 600, 650 and 700 °C. During the growth of VACNTs, the reaction time was 30 min, the gas inlet contained ethylene (70 cm^3/min) as carbon source, nitrogen (50 cm^3/min) as carrier gas, hydrogen (50 cm^3/min) for the reducing environment and water vapor (25 cm^3/min) to prolong the activity of the catalyst particles.

Results and discussion

Due to the lack of information in the literature on VACNT synthesis on AZO substrate, experiments were conducted at three different synthesis temperatures, with seven different Fe:Co catalyst ratios, in the absence and presence of Al_2O_3 support layer, to study the effect of synthesis parameters on the properties of VACNTs.

During the first set of experiments, the development of carbon deposition was studied as a function of reaction temperature and catalyst composition in the absence of Al_2O_3 support layer. The following conclusions can be drawn from the results: no carbon deposition was observed on the AZO substrate surface in case of using only pure cobalt as a catalyst at 600, 650 and 700 °C; similar results were achieved at 700 °C for the pure iron catalyst in the absence of the support layer, and neither carbon deposition nor CNT growth was significant for the pure iron catalyst at other temperatures, at 600 °C, mainly amorphous carbon, carbon fibres and coiled CNTs were identified, at higher temperatures CNTs were formed randomly in larger bundles on the AZO surface. The series of experiments were repeated in the presence of Al_2O_3 support layer and the following results were obtained: all three synthesis temperatures resulted in significant evolution in the presence of support layer, and carbon nanotubes were apparently formed, however, at 600 °C the carbon nanotubes were still not aligned, at 650 °C, obviously vertically aligned carbon nanotubes were observed on the surface of AZO substrate surface at all catalyst ratios, and at 700 °C, besides the pure iron catalyst, also VACNTs were formed. In this work, short carbon nanotubes were grown, with the highest average height of VACNTs (9.0 μm and 8.7 μm) achieved at 650 °C for Fe:Co 2:3 and at 700 °C for Fe:Co 1:3, which is

an additional difference from previous studies that the highest carbon nanotubes were not formed at the 1:1 catalyst composition [19]. Application of the support layer was beneficial during the synthesis as it was assumed to inhibit the aggregation and diffusion of catalyst particles, which ensured a homogeneous distribution of catalyst nanoparticles on the surface. This claim was verified by performing blank syntheses in which hydrogen gas was circulated in the system for 5 minutes without the carbon source. In order to confirm the graphitic properties, the samples synthesised in the second experimental series were analysed by TEM and Raman spectroscopy. Based on the results, the following conclusions were drawn: multi-walled CNTs were grown during the CCVD process, with the number of walls varying between 7 and 10, with irregularities in the walls, suggesting that the CNTs contain numerous defect sites in the structure, which indirectly predicts that the graphitic and conductive properties of the CNTs might be average.

Theoretical considerations have confirmed that the nitrate compounds used to prepare support and catalyst layers were unstable thus annealing the nitrate precursors at 400 °C for 1 h indeed ensures the formation of the desired oxides, which was our goal. Based on the results, it was found that at all three synthesis temperatures (600, 650, 700°C), Fe_2O_3 and CoO layers were reduced to metallic iron and cobalt under the influence of hydrogen gas, and even the ZnO in the AZO layer was reduced to metallic zinc under the influence of hydrogen gas, whereas the support layer was stable, not reduced to elemental aluminum. The reduction of the surface ZnO layer of AZO to elemental zinc at the synthesis temperature under the influence of hydrogen gas resulted in both melting and the reaction with the reduced cobalt and iron nanoparticles, which led to the formation of intermetallic compounds, and therefore the iron and cobalt nanoparticles lost their catalytic properties. Presumably this was the case in the first series of experiments in the absence of support layer. Under the synthesis conditions used, iron-cobalt bimetallic catalysts formed bcc phase iron-cobalt solid solutions on the AZO surface in the presence of the support layer, which, due to interface effects, formed a core-shell structure, where iron formed the shell and cobalt the core. The solubility and diffusion rates of carbon atoms in iron are higher than in cobalt, resulting in the hollow structure characteristic of CNTs.

Conclusion

The conclusion is that Al_2O_3 support layer and iron-cobalt bimetallic catalyst layer are essential to synthetize VACNTs on AZO substrate. Based on experimental and theoretical results, it has been confirmed that a multi-walled CNT forest can be grown on AZO substrate by dip coating a bimetallic catalyst layer and an alumina support layer at 650 and 700 °C. It is confirmed that at CCVD synthesis temperature, in the presence of hydrogen gas, the initial iron and cobalt oxides were reduced to iron and cobalt metals, while Al_2O_3 remained stable and therefore able to fulfill the role of the support layer. On the basis of thermodynamic considerations, the bcc crystalline structured biphasic iron-cobalt nanoparticles formed core/shell structures in the presence of a support layer on AZO substrate.

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