PREPARATION AND CHARACTERIZATION OF ONE-DIMENSIONAL NANOSTRUCTURES

Ph.D. thesis

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1. Introduction

For the last couple of years the one-dimensional (1D) nanostructures (nanowires, nanorods, nanotubes etc.) have gained steadily growing interest in the field of nanotechnology. In comparison with the 0 dimensional nanostructures, such as quantum dots and nanoparticles, 1D nanostructures could be better models for the investigation of the dependence of electronic transport, optical and mechanical properties on dimensionality and quantum confinement. Though certain nanowires could prove to be suitable as part of nanodevices, until very recently this field of nanotechnology advanced relatively slowly on account of the lack of nanostructures with well-controlled size, crystallinity and chemical composition, etc. Accordingly, more and more research, such as the present work, has been focused on the synthesis, characterization and application of 1D nanostructures with well-controlled properties.

In general, the preparation of 1D nanostructures in particular is all about constraining the growth of material in two directions to the nanometer scale and facilitate the growth in the third direction. In fact, 1D growth can be carried out either physically or chemically by breaking the growth symmetry of a material. Nowadays several methods are available for the synthesis of 1D nanostructures. Most of them are based on the application of linear templates, for example: porous membranes, surfactants, nanofibers, etc.

At the same time, there are some alternative approaches. One of them, for instance, is controlling crystal growth by the size of the catalyst applied. These procedures are called by the phase used during the synthesis, eg.: vapour-liquid-solid (VLS) growth. Notwithstanding that there exist a number of techniques; there is still a huge gap between successful applications and technologies. Most of all processes applicable on the industrial scale with the ability to be run cost-effectively and be automated, etc. are needed.

For the last couple of years at the Department of Applied and Environmental Chemistry, 1D nanostructures of different materials have been successfully prepared and the properties and potential applicability of carbon and titanate nanotubes and nanowires have been explored. Joining in this work the primary objective of this Ph.D. thesis has been set as follows: preparation and characterization of 1D metallic nanostructures, investigation of their potential applicability, and studying the galvanic exchange reaction on 1D metallic nanostructures. Furthermore, in addition to this research my goal was to broaden knowledge in the following research areas:

1. Synthesis of 1D noble metal nanostructures with high specific surface area and porous structure using the galvanic exchange reaction on nickel nanorods. Investigation of the catalytic activities of the noble metal nanorods in the model reaction of ethylene hydrogenation.
2. Development of a method applicable for the preparation of copper nanowires in a relatively large-scale.
3. Revealing the formation and growth mechanism of copper nanowires.
4. Performing the electrical characterization of copper nanowires.
5. Preparation of platinum and palladium nanotubes on copper nanowires by galvanic exchange reaction.

Experimental

Nickel nanorods were grown by electrodeposition technique in porous alumina (AAO) template. Using a three electrode potentiostate system (Autolab) for the electrochemical deposition of nickel, platinum wire counter electrode and Ag/AgCl reference electrode was used. After purging the nickel sulfate solution with argon gas, deposition was carried out at constant potential (−1.0 V) for 1−1.5 h from a solution of 0.2 M nickel sulfate and 0.1 M boric acid in AAO template. After dissolving the template material, the nickel nanorods were washed and centrifuged several times. Scanning electron microscopy was used for morphological characterization of nanorods.

After treating the nanorods with hydrazine monohydrate the nanostructures were immersed either into a 0.01 M solution of $HAuCl_4$ or K_2PdCl_4 or H_2PtCl_6. The reaction was accompanied by slow stirring. After completion of the reaction, the porous noble metal nanorods were separated from solution by centrifugation and redispersed again in double distilled water. The samples prepared this way were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analysis. The surface area measurements were carried out in an automatic N_2 adsorption equipment. Catalytic activities of platinum and palladium catalysts were investigated in the model reaction of ethylene hydrogenation. The reaction products were analyzed by gas chromatography.

Copper nanowires have been prepared by a novel hydrothermal route and their morphology has been characterized by transmission (TEM) and scanning electron microscopy (SEM). XRD and electron diffraction (ED) patterns were used to analyze the crystalline nature of the nanostructures. Based on the above mentioned methods we have attempted to reveal the growth mechanism of the copper nanowires. Furthermore, electrical properties of the nanowires have been examined. For the electrical measurements, copper nanowires were dispersed in ethanol, sonicated, and drop-casted on a Si/SiO_2 chip equipped with Pt/Ti electrodes. A Keithley 2636A sourcemeter was used in all resistance−temperature, current−voltage, and resistance−gate voltage measurements. All the current−temperature and current−voltage measurements were performed in a Linkam THMS600 heating and freezing stage applying 6 K/min heating and cooling rates.

CuPd and CuPt bimetallic nanotubes have been prepared by using the galvanic replacement reaction. The nanotubes were characterized by electron microscopy. The chemical composition of the nanowires was analyzed by EDS measurements, while to determine their crystallinity XRD was used.

3. New scientific results

1. Synthesis of noble metal nanostructures and their catalytic testing in ethylene hydrogenation reactions.

1.1 A novel method has been invented for the preparation of porous Au, Pt, and Pd nanorods by improving the well-known galvanic exchange reaction. The rather expensive silver template has been substituted with nickel nanorods generated by electrodeposition.

1.2 The formation of porous nanostuctures has been examined by SEM, EDS, XRD and XPS techniques. The specific surface areas of the Au, Pd, and Pt nanorods were determined by N_2 adsorption-desorption measurements and was found to be about 30 m^2/g. The specific surface area of porous nanorods is comparable with that of commercially available platinum black powder (20-26 m^2 /g). Based on the SEM images, the average diameters were found to be 304 ± 77, 259 ± 69, and 284 ± 79 nm for Au, Pt, and Pd rods, respectively. The differences in the sizes of Au, Pt, and Pd have not been analyzed fully; however, it is suggested that the oxidation states of the precursors are responsible for this phenomenon.

1.3 It should be emphasized that the nanorod preparation process described by us is free from any surfactants; therefore, all potentially active metal sites are available for catalytic reactions. The catalytic activities of the porous Pt and Pd nanorods were investigated in the model reaction of hydrogenation of ethylene. The apparent activation energies for Pt and Pd nanowires were found to be 43.7 ± 1.7 kJ mol^{-1} and 29.4 ± 1.3 kJ mol^{-1}, respectively. They proved to be nearly identical with those found in literature for ethylene hydrogenation on supported Pd revealing comparable efficiency of porous rods with supported nanoparticles.

1.4 Palladium nanoparticles (4.8 ± 0.6 nm) have been synthesized in polydimethysiloxane (PDMS) matrix. The apparent activation energies (2.4 and 2.3 kcal/mol) of ethylene hydrogenation on PDMS membranes containing 1 and 2 wt% of Pd nanoparticles have been determined.

2. Results related to copper nanowires: method of preparation, formation mechanism and electrical properties.

2.1 Novel hydrothermal method has been elaborated for the preparation of copper nanowires that can be characterized with a length of several micrometers and an aspect ratio of >50.

2.2 The nanowires were investigated by TEM, ED, SEM, EDS, and XRD. The microscopic images showed that the Cu NWs had a uniform diameter of 64 ± 8 nm.

The electron diffraction (ED) analysis revealed and proved that the nanowires were single crystals.

2.3 In order to assess the optimal ratio of glucose/HDA/$CuCl_2$ needed to obtain a final product composed mostly of NWs, the role of 1-hexadecylamine (HDA) and glucose has been investigated by a series of experiments.

2.4 In order to understand the growth mechanism of copper nanowires, hydrothermal syntheses of various durations were performed to gain insight into the growth kinetics of copper nanowires. In the case of 1 hour synthesis the samples were mostly composed of 2.1±0.7 nm copper nanoparticles and hardly any nanowires appeared. At this early stage, the HDA was observable as planes in the TEM images. On increasing the synthesis period to 2 and 3 hours, some copper nanowires showed up and the structure of HDA appeared rather to be coiled than planar. Based on our investigations we have suggested a possible mechanism: the initial formation of nanoparticles is followed by the growth of NWs at later stages.

2.5 The electrical properties of copper NWs have been measured using oxidative/reductive atmospheres and heating cycles. Samples were treated in oxidative–reductive atmospheres in the following heat cycles with a rate of 6 K/min: 300 K → 550 K → 350 K → 550 K → 300 K. It was assessed that the sample could not be reduced and re-oxidized again after the first oxidation-reduction cycle.

3. Results on the formation of CuPt and CuPt bimetallic nanotubes by galvanic replacement reaction.

3.1 We have developed a new method for the preparation of CuPd and CuPt bimetallic nanotubes (NTs) by applying the galvanic replacement reaction.

3.2 The TEM, SEM, EDS, and ED measurements revealed formation of etch pits on the surface of the NWs. Electron microscopy studies shed light on the different behaviour of the two systems. When exchanging copper with Pt, a slight increase in size was experienced, while on adding only a small amount of $PdCl_4^{2-}$, the CuPd exchange lead to the formation of significantly thicker nanotubes.

3.3 In the case of Cu−Pt exchange, based on the XRD analysis, it has been suggested that Pt probably diffuses into the copper to form CuPt alloy. Upon adding more and more K_2PtCl_4 solution to the system the Pt content increases until about 66 %, that is, the copper content of the NWs (~33 atomic %) cannot be further decreased. Contrary to this phenomenon, the Cu−Pd metal exchange reaction resulted in a much lower copper content (~2-3 atomic %) and no formation of CuPd alloy was shown by XRD analysis.

4. Practical applicability of the results

The results presented are likely to be significant mainly in the field of fundamental research. However, the materials synthesized in our lab could be potentially further developed and used in several areas.

The most important fields for potential application are as follows:

- The metallic nanowires can prove to be potential candidates as building blocks in electrical devices due to their high electrical conductivity.
- The porous nanowires, owing to their high specific surface area, first of all, could be applied in the field of catalysis and sensing.
- The CuPt and CuPd bimetallic nanowires, due to their high activity toward redox reactions, could be applied as catalysts of the redox processes in proton-exchange membrane fuel cells (PEMFCs).

5. Papers related to the present thesis

1. **Synthesis of catalytic porous metallic nanorods by galvanic exchange reaction**
   M. Mohl, A. Kumar, A. L. Mohana Reddy, A. Kukovecz, Z. Konya, I. Kiricsi, R. Vajtai and P. M. Ajayan,
   Journal of Physical Chemistry C, 2010, 114 (1), 389–393
   IF $_{2009}$: 4.224, independent citations: 1

2. **Low-temperature large-scale synthesis and electrical testing of ultralong copper nanowires**
   M. Mohl, P. Pusztai, A. Kukovecz, Z. Konya, J. Kukkola, K. Kordas, R. Vajtai, P. M. Ajayan
   Langmuir 2010, 26 (21), 16496-16502
   IF $_{2009}$: 3.898

3. **In-situ synthesis of catalytic, metal nanoparticle-PDMS membranes by thermal decomposition process**
   A. Goyal, A. Kumar, **M. Mohl**, R. Puskas, A. Kukovecz, Z. Konya, I. Kiricsi, P. M. Ajayan
   Composites Science and Technology, 2011, 71 (2), 129–133
   IF $_{2009}$: 2.901

4. **Formation of CuPd and CuPt bimetallic nanotubes by galvanic replacement reaction**
   M. Mohl, D. Dobo, A. Kukovecz, Z. Konya, K. Kordas, J. Wei, R. Vajtai, P. M. Ajayan
   Journal of Physical Chemistry C, (accepted for publication)
   IF $_{2009}$: 4.224

6. Presentations, posters, attending conferences

1. **Catalytic treatment of chlorobenzene and chlorobenzene derivatives**

   M. Mohl, Sz. Mészáros and J. Halász

   8th International Symposium on Interdisciplinary Regional Research,

   Hungary-Romania-Serbia and Montenegro, Szeged, Hungary, 19-21 of April 2005 (presentation and poster)

2. **Új típusú mikrofluidikai reaktor használata a szintetikus kémiában (Use of a new type of microfluidic reactor in synthetic chemisrty)**

   K. Niesz, I. Hornyák, Cs. Csajági, I. Kovács, B. Borcsek, D. Szalay, **M. Mohl**, Z. Kónya, I. Kiricsi, L. Ürge, F. Darvas

   MKE Centenary Conference, Sopron, Hungary 2007 (poster)

3. **Synthesis and characterisation of large pore volume mesoporous carbon**

   E. Horvath, R. Puskas, **M. Mohl**, A. Kukovecz, Z. Kónya, I. Kiricsi

   Carbon for Energy Storage and Environment Protection –CESEP, Krakow, Poland 2007 (poster)

4. **Functionalization of multi-walled carbon nanotubes (MWCNTs)**

   M. Mohl, A. Kukovecz, Z. Kónya, I. Kiricsi

   NATO-Advance Study Institute, Sinaia, Romania, 2008 (presentation and poster)

   Awarded poster

5. **Electrical properties and gas sensitivity of nickel-palladium nanowire thin films**

   J. Kukkola, J. Mäklin, N. Halonen, K. Kordás, **M. Mohl**, A. Sapi, A. Kukovecz, Z. Konya, I. Kiricsi, A. Kumar, A. L. Mohana Reddy, R. Vajtai, P. M. Ajayan

   Nanoscience days, Jyväskylä, Finland, 2009 (poster)

6. **Electron microscopic study of various metal nanostructures**

   M. Mohl, A. Kukovecz, Z. Kónya, I. Kiricsi

   Hungarian Society for Microscopy, Siófok, Hungary, 2010. Annual Meeting (presentation)

7. Other publications

1. **Catalytic treatment of chlorobenzene and chlorobenzene derivatives**
   M. Mohl, M. Mészáros and J. Halász
   Annals of the Faculty of Engineering HUNEDOARA, 2006, Tome IV, Fascicole 3
   ISSN: 1584 – 2673

2. **Morphology and N_2 permeability of multi-wall carbon nanotube– Teflon membranes**
   R. Smajda, A. Kukovecz, B. Hopp, **M. Mohl**, Z. Kónya, I. Kiricsi
   Journal of Nanoscience and Nanotechnology 2007, 7, 1604-1610
   IF_{2009}: 1.435, independent citations: 2

3. **Functionalization of multi-walled carbon nanotubes (MWCNTs)**
   M. Mohl, A. Kukovecz, Z. Kónya, I. Kiricsi
   NATO Science for Peace and Security Series B: Physics and Biophysics Functionalized Nanoscale Materials, Devices and Systems (A. Vaseashta and I. N. Mihailescu, eds.)
   2008, pp. 365-368
   ISBN: 978-1-4020-8902-2 (Print) 978-1-4020-8903-9
   (Online) DOI: 10.1007/978-1-4020-8903-9_32 ISSN: 1874-6500

4. **A Novel catalyst type containing noble metal nanoparticles supported on mesoporous carbon - synthesis, characterization and catalytic properties**
   E. Horváth, R. Puskás, R. Rémiás, **M. Mohl**, A. Kukovecz, Z. Kónya, I. Kiricsi
   Topics in Catalysis, 2009, 52 (9), 1242-1250
   IF_{2009}: 2.379

5. **Improving the performance of functionalized carbon nanotube thin film sensors by fluctuation enhanced sensing**
   A. Kukovecz, P. Heszler, K. Kordas, S. Roth, Z. Kónya, H. Haspel, R. Ionescu, A. Sápi, J. Maklin, **M. Mohl**, Z. Gingl, R. Vajtai, I. Kiricsi, P. M. Ajayan
   Proceedings of the SPIE, 2008, 7037, pp. 70370Y-70370Y-10

6. **Increasing chemical selectivity of carbon nanotube-based sensors by fluctuation-enhanced sensing**

   D. Molnar, P. Heszler, R. Mingesz, Z. Gingl, A. Kukovecz, Z. Konya, H. Haspel, **M. Mohl**, A. Sapi, I. Kiricsi, K. Kordas, J. Mäklin, N. Halonen, G. Toth, H. Moilanen, S. Roth, R.Vajtai, P.M. Ajayan, Y. Pouillon, and A. Rubio

   Fluctuation and Noise Letters, 2010, 9 (3), 277–287

   IF $_{2009}$: 0.46

7. **Carbon nanotube based sensors and fluctuation enhanced sensing**

   A. Kukovecz, D. Molnár, K. Kordás, Z. Gingl, H. Moilanen, R. Mingesz, Z. Kónya, J. Mäklin, N. Halonen, G. Tóth, H. Haspel, P. Heszler, **M. Mohl**, A. Sápi, S. Roth, R.Vajtai, P.M. Ajayan, Y. Pouillon, A. Rubio, I. Kiricsi

   Physica Status Solidi C, 2010, 7 (3-4), 1217–1221

   IF $_{2009}$: –

Peer-reviewed papers total: 11,	out of this, related to the topic of thesis: 4
Cumulative impact factor: 19.521,	out of this, related to the topic of thesis: 15.247
Independent cites total: 3,	out of this, related to the topic of thesis: 1