PREPARATION AND CHARACTERIZATION OF A MULTIFUNCTIONAL POLYMER REINFORCING NANOMATERIAL

Ph.D. thesis

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Szeged

2009

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1. Introduction

Nowadays this is the era of global competition for possessing state-of-the-art technologies and hence, there is a huge interest in the preparation and characterization of novel 1D nanoparticles such as nanotubes and nanofibres because of their unique optical, electrical and mechanical properties.

The synthesis and characterization of high-aspect-ratio titanium oxide nanostructures have commended considerable attention recently owing to their wide range of potential applications. There is a rapidly growing number of research groups who adopted this topic in their profile recently. It is nearly a decade now since the very simple, low-cost, easily up-scalable and adjustable alkali hydrothermal titanate synthesis method has been developed. The recipes for preparing the two different morphologies (tube-like and wire-like titanates) became known to the scientific community nearly at the same time. However, regarding the number of publications and their distribution in contemporary literature later research efforts drifted towards the investigation of the nanotube morphology which perhaps has more exciting opportunities compared to the wire-like form. It is no surprise, therefore, that even though certain elements of the scientific puzzle of titanate nanowire chemical structure and formation mechanism are available, different research groups assembled dissimilar pictures from the parts.

Since the special properties of nanomaterials are strongly size-dependent, the prerequisite for their practical application is gaining reliable control over their particle size and shape in the production phase.

My objective in this Ph. D. thesis was to explore the potentials of the simple alkali hydrothermal titanate nanomaterial synthesis, in particular by doing research on reducing manufacturing costs and ameliorating the process tunability. The main work was done in the following themes:

1. Finding an economically more advantageous synthesis method which leads to a crystallographically and morphologically uniform product:
    - Modification of traditional hydrothermal nanowire production process
    - Designing of a special rotating autoclave unit

2. Characterization of titanate nanowires:
    - Determination of the physical and chemical properties

3. Studies on the formation mechanism:
    - Monitoring the nanowire formation process as a function of time by TEM, HRTEM, SEM, XRD and FT-Raman methods and determine the specific surface of by N_2 adsorption measurement
    - Revealing the chemical relationship between the nanotube and the nanowire form
    - Demonstrating the effect of starting material on the physical and chemical properties of titanate nanostructures produced via the modified synthesis
4. Examining, whether the anisotropic nanoobjects could be used as polymer reinforcing nanofillers:
    - Embedding the titanate nanowires into two different polymer matrices by using two different methods
    - Surface modification of titanate nanostructures in order to get better dispersion in polymer matrix
    - Determination the mechanical and thermal properties of titanate-polymer nanocomposites
    - Find the optimal polymer reinforcing material

2. Experimental

Titanate nanotubes were prepared by the alkaline hydrothermal method discovered by Kasuga et al. 2 g of titanium (IV) oxide (anatase) was mixed with 140 ml of 10 M sodium hydroxide solution, while milky white suspension was obtained. The mixture was transferred into a 180 ml volume Teflon-lined stainless steel autoclave then placed in a 130 ° C preheated oven for 24 h. After cooling to room temperature the product was filtered, washed with distilled water until pH 8 was reached and dried in air.

The nanowire preparation was performed by analogy with the above-mentioned formulation in a self-developed Teflon-lined autoclave unit equipped with special flow pattern breaking fittings which was rotated 0.1-140 RPM around its short axis.

The shape and the size of the obtained nanotubes and nanofibres were characterized by transmission electron microscopy. The changes in the crystal structure during the formation were monitored with X-ray diffraction and FT-Raman spectroscopy and the specific surface area of the samples were determined by N_2 adsorption measurement.

Taking advantage of their cation exchange properties we have succeeded in surface modification of titanate nanostructures with hydrophobic magnesium stearate in aqueous media. FT-IR spectroscopy was used for the qualitative identification of surface modifier and thermogravimetric analysis was used to determine the quantity of the soap. Floating test and contact angle analysis indicated that the final titanate obtained was hydrophobic.

We used polymer melt intercalation process to produce high density polyethylene (HDPE) titanate nanowire nanocomposites in Brabender plastograph. The melt blending was performed at 170 °C. More polyurethane titanate nano-composites have been created with drop casting method. The mechanical reinforcement was concluded as a result of the tensile test measurements.

3. New scientific results

1. Results on the preparation of anisotroph titanate nanostructures

1.1 A new hydrothermal titanate nanotube and nanowire production process and setup were developed which are distinctly different from the currently used traditional method. The improved process is based on a new rotating autoclave unit. The autoclave's RPM can be adjusted to produce different types of products and to modify several characteristics. The instrument contains special flow pattern breaking fittings that prevent the sedimentation of the product during the synthesis. We found that with our modified process the nanowires can be manufactured at a lower temperature using a milder alkali environment ($T \leq 130$ ° C, cNaOH = 10 M). Furthermore, taking the volume of the reaction vessel into account there is an approximately ten-fold increase in yield as compared to the conventional hydrothermal method, because of the more effective volume leverage. The obtained product is a sponge-like, soft material, hence can be handled more easily during the subsequent application phases.

1.2 The nanowire formation process was monitored as a function of time by TEM, HRTEM, SEM, XRD and FT-Raman methods and the specific surface area of the samples was determined by N_2 adsorption measurements. As a result of the detailed formation mechanism investigation we first noticed that the nanowires are formed from self-assembled nanotube bundles. Based on the results, the mixing-force-assisted "oriented attachment" nanowire formation was proposed.

1.3 The metastable transient nature of trititanate nanotubes was directly demonstrated using nanotubes instead of anatase nanoparticles as starting material for the nanowire synthesis. With this procedure the titanate nanowire's length-to-width (diameter) ratio, crystallinity and specific surface area (20-350 m^2/g) can be more precisely controlled.

1.4 We created a novel material containing a parallel, longitudinal array of mesoporous titanate nanowire channels. This material is anticipated to find many applications as adsorbent and catalyst support.

2. Results about the modified anisotropic titanate nanostructures

2.1 Taking advantage of the cation exchange properties of titanate nanostructures a simple hydrophobization method has been successfully set up using magnesium stearate as surface modifier. FT-IR spectroscopy was used for the qualitative identification and thermogravimetric analysis was used to determine the quantity of the surfactant. On the basis of these measurements we successfully rendered the hydrophilic nanowire surface hydrophobic. The magnesium stearate content of surface modified samples was 10.8-11.7 w/w%. Contact angle and floating test measurements were performed in order to demonstrate the hydrophobicity. It has been shown that the surface modified samples exhibit superhydrophobic properties.

3. Results related to applications of anisotropic titanate

3.1 We have examined first in this field whether the hydrothermally synthesized titanate nanostructures are capable of strengthening polymer matrices. We performed preliminary experiments on high density polyethylene (HDPE) titanate nanowire nanocomposites prepared in a Brabender plastograph. The tensile tests results (namely, the increasing yield strength and Young modulus combined with the decreasing tensile strength and strain at break) showed us that nanowires can influence the mechanical properties of the composites positively.

3.2 Three types of titanates with different aspect ratio, crystallinity and specific surface area as well as their magnesium stearate surface modified counterparts were embedded into thermoplastic polyurethane using the drop casting method. We observed that the nanowire sample with the highest aspect ratio had a superior reinforcing effect on the polyurethane matrix. On the basis of previous results we conclude that when using the proper procedure, anisotropic titanate nanostructures are suitable materials for the production of reinforced polymer nanocomposites. The crystallinity and thermal properties of the polyurethane-titanate nanocomposites were characterized by XRD, TG and DSC methods.

4. Practical applicability of the results

During the compilation of the presented work the main guiding principle was not only to discuss the necessary basic research results, but to outline a few potential application areas as a *know how*. As a result of the University of Szeged and its partners' effective innovation activity, two Hungarian patent applications and one Hungarian utility model protection have been submitted related to this thesis. Once these applications get accepted eventually, this work could then contribute to the entire exploitation of their widespread potentials.

The most important potential applications are as follows:

- Utilization of the anisotropic titanate nanoparticles as polymer filler material. Besides serving as a reinforcing and UV protecting agent, the filler could double as a white pigment as well. The bioinert and bioactive properties of titanate nanoparticles can inspire applications in the medical and pharmaceutical field.

- Since anisotropic titanate nanoparticles can be sensitized and rendered photoactive, their polymer nanocomposites can be utilized to create self-cleaning membranes and textiles. The main interest for their practical applicability is coming from the textile industry, however, titanate nanotube/nanowire polymer nanocomposite membranes may also find applications in various air, water and wastewater treatment technologies.

5. Papers related to the present thesis

1. **Hydrothermal conversion of self-assembled titanate nanotubes into nanowires in a revolving autoclave**

   E. Horvath, A. Kukovecz, Z. Konya, I. Kiricsi

   Chemistry of Materials **19** (2007) 927-931

   IF: 4.885, independent citations: 15

2. **Chemical functionalisation of titania nanotubes and their utilisation for the fabrication of reinforced polystyrene composites**

   JE. McCarthy, M. Bent, R. Blake, YK. Gun'ko, E. Horvath, Z. Konya, A. Kukovecz, I. Kiricsi, JN. Coleman

   Journal of Materials Chemistry **17** (22) 2351-2358

   IF: 4.339, independent citations: 10

3. **Fine tuning the coverage of a titanate nanowire layer on a glass substrate**

   M. Darányi, Á. Kukovecz, E. Horváth, Z. Kónya, I. Kiricsi

   Chemical Physics Letters **460** (2008) 191-195

   IF: 2.207, independent citations: 0

4. **Titanate-polimer nanocomposite and method for producing the same**

   Cs. Cserháti, Z. Csernátony, L. Daróczi, Gy. Deák, E. Horváth, S. Kéki, I. Kiricsi, Z. Kónya, Á. Kukovecz, M. Zsuga

   P0700484 hungarian patent

5. **Apparatus for producing titanate nanostructures**

   Dr. I. Kiricsi, Dr Á. Kukovecz , Dr. Z. Kónya, E. Horváth

   U 07 00228, PCT/HU08/000155 hungarian utility model protection

6. **Titanate nanowire and method for producing the same**

   Dr. I. Kiricsi, Dr Á. Kukovecz , Dr. Z. Kónya, E. Horváth

   P 0700839 hungarian patent application

6. Talks and posters related to the present thesis

1. **On the formation of titanate nanowires**
   E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi
   SM-2005 School of Ceramics
   Novi Sad, Serbia and Montenegro, December 1-2, 2005, (oral)

2. **Polymer nanocomposites based on titanate nanostructures**
   E. Horváth, Á. Kukovecz, Z. Kónya, Gy. Deák, M. Zsuga, I. Kiricsi
   Materials Science committee of the Hungarian Academy of Sciences
   Debrecen, 2006 spring meeting (oral)

3. **Polymer nanocomposites based on titanate nanostructures**
   E. Horváth, Á. Kukovecz, Z. Kónya, Gy. Deák, M. Zsuga, I. Kiricsi
   3rd China-Europe Composite Symposium
   Budapest, Hungary, 11-15 June 2007 (poster)

4. **From macaroni into fettuccini? a non-classical crystal growth mechanism**
   E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi
   XXX. KEN, Chemistry Lecture Days
   Szeged, 29-31 October 2007 (oral)

7. Other publications

1. **Photosensitization of ion-exchangeable titanate nanotubes by CdS nanoparticles**
   M. Hodos, E. Horváth, H. Haspel, Á. Kukovecz, Z. Kónya, I. Kiricsi
   Chemical Physics Letters **399** (2004) 512-515
   IF: 2.438, independent citations: 46

2. **Vibrational spectroscopic studies on the formation of ion exchangeable titania nanotubes**
   M. Hodos, H. Haspel, E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi
   XIX. Winterschoool on Electronic Properties of Novel Materials, 2005, Kirchberg in Tirol
   Proceedings of the XIX. Winterschool on Electronic Properties of Novel Materials
   (Edited by H. Kuzmany, J. Fink, M. Mehring)
   AIP Conference Proceedings **786** (2005) 345-348

3. **Oriented crystal growth model explains the formation of titania nanotubes**
   Á. Kukovecz, M. Hodos, E. Horváth, Gy. Radnóczi, Z. Kónya, I. Kiricsi
   Journal of Physical Chemistry B **109** (2005) 17781-17783
   IF: 4.033, independent citations: 38

4. **Tubular inorganic nanostructures**
   I. Kiricsi, Á. Fudala, D. Méhn, Á. Kukovecz, Z. Kónya, M. Hodos, E. Horváth, M. Urbán, T. Kanyó, É. Molnár, R. Smajda
   Current Applied Physics **6** (2006) 212-215
   IF: 1.116, independent citations: 2

5. **On the morphology and transport properties of HDPE–titanate nanowire nanocomposites**
   J. Szel, E. Horvath, A. Sapi, H. Haspel, A. Kukovecz, Z. Konya, I. Kiricsi
   IWEPNM 2007
   Kirchberg in Tirol, Austria, March 10-17, 2007 (poster)

6. **Synthesis and characterisation of large pore volume mesoporous carbon**
   E. Horváth, R. Puskás, R. Rémiás, M. Mohl, A. Kukovecz, Z. Kónya, I. Kiricsi
   Carbon for Energy Storage and Environment Protection -CESEP´07
   Krakow, Poland, September 2-6, 2007 (poster)

7. **Synthesis and characterisation of noble metal nanoparticles supported in the pore system of mesoporous carbon**
   E. Horváth, R. Puskás, R. Rémiás, Á. Kukovecz, Z. Kónya, I. Kiricsi
   IX. Pannonian International Symposium on Catalysis,
   Strbske pleso, Slovakia September 8-12, 2008 (poster)

8. **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, G. A. Somorjai, I. Kiricsi
   Topics in Catalysis **52** (2009) 1242-1250
   IF: 2.212, independent citations: 0

9. **Subacute intratracheal exposure of rats to manganese nanoparticles: Behavioral, electrophysiological, and general toxicological effects**
   L. Sárközi, E. Horváth, Z. Kónya, I. Kiricsi, B. Szalay, T. Vezér, A. Papp
   Inhalation Toxicology, **21** (2009) 83-91
   IF: 2.403, independent citations: 0

10. **Neurotoxic effects of metal oxide nanoparticles on the somatosensory system of rats following subacute intratracheal application**
   L. Sárközi, E. Horváth, A. Szabó, E. Horváth, A. Sápi, G. Kozma, Z. Kónya, A. Papp
   Neurotoxicity of Metal Oxide Nanoparticles, **14** (2008) 277-290
   IF: - , independent citations: 0

Peer-reviewed papers total: 10,	out of this, related to the topic of thesis: 3
Cumulative impact factor: 23.633,	out of this, related to the topic of thesis: 11.431
Independent cites total: 111,	out of this, related to the topic of thesis: 25