# INVESTIGATIONS ON THE MECHANOCHEMICAL SYNTHESIS AND MODIFICATION POSSIBILITIES OF NANOSTRUCTURES

Ph.D. thesis

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# 1. Introduction and aims

Today's technological demands require the large scale production of the most advanced materials available. Nanotechnology, one of the most fashionable scientific areas of the past decade, provides solutions for this. Particles in the nanometer size range (nanomaterials) owe their outstanding usability to physico-chemical properties that are markedly different from those of the corresponding bulk phases. Moreover, these materials can be prepared in several different morphologies corresponding to 0, 1 and 2-dimensional nanostructures. The lattice constant and surface energy of nanomaterials differs from those of bulk materials. Their specific surface area is significantly larger, which results in high surface energy and surface-to-volume ratio. Nanomaterial based technologies are expected to be utilized in new production technologies that can replace the current non-sustainable ones according to the needs of our time. One of the prerequisites for this is to produce nanomaterials in sufficiently large quantities.

Basically, two approaches are available for manufacturing nanostructures: top-down and bottom-up. These utilize the size reduction of a bulk material or the assembly of atoms and ions to yield nanoparticles, respectively. Both approaches are open for mechanochemistry, which essentially means the use of mechanical energy to initiate processes leading to desired products. The two groups of potential processes are: 1) synthesis of new materials from precursors by mechanical activation, 2) modification of existing structures to obtain materials with new properties. The main advantages of mechanochemistry over other competitive methods from the industrial point of view are the following. 1) It renders reactions with high activation energy feasible without necessitating significant changes to the bulk temperature of the reaction mixture. 2) The equipment most suitable for mechanochemical reactions (i.e. the ball mill) is well-known and widely used in the chemical industry, therefore, mechanochemistry–based nanomaterial production methods can spread quickly and without major capital investments.

The Department of Applied and Environmental Chemistry has been actively developing nanostructure synthesis methods and applications in the past two decades. Our group mainly focuses on one-dimensional carbon and titanate nanostructures and zero dimensional metals and metal oxides. The objective of my doctoral research was to introduce mechanochemistry

into this field in general, and to survey its applicability for the synthesis and modification of such nanoparticles in particular. The following topics were covered by my work:

We verified the applicability of the Burgo-Rojac model for calculating the energy transferred to milled nanomaterials in a planetary ball mill.

We studied the mechanochemical modification of carbon nanotubes and one-dimensional titanate nanostructures. The relationship between certain properties of carbon nanotubes and mechanical energy transfer was uncovered. Moreover, we observed changes in the mechanical, structural and surface properties of titanate nanostructures (tubes and wires) upon treatment in a planetary ball mill.

We monitored the temporal evolution of temperature and pressure during mechanochemical reactions in situ in the milling drum by using a special detector head. The obtained data was useful for deepening our understanding of mechanochemical reaction kinetics and also for optimizing the reaction time.

We synthesized metal-oxide nanoparticles in a planetary ball mill based on a general synthesis method optimized by us. The obtained materials were characterized both from the structural and from the reproducibility points of view.

## Experimental

A Fritsch Pulverisette-6 type planetary ball mill was used for the grinding experiments with the following accessories: 1) a $Si_3N_4$ (silicon-nitride) and 2) a Fe-Ni-Cr (stainless steel) grinding bowl with volumes of 80 mL and 3) 250 mL, 4) 10 mm diameter $Si_3N_4$ and 5) 10 and 5 mm diameter Fe-Ni-Cr grinding balls. The rotational speed was variable between 100 and 650 rpm. The total duration of milling and the rotational direction were also varied. The most important accessory of the system was the GTM-II (Gas pressure and temperature measuring system) detector head, which is able to monitor pressure and temperature changes in situ and relay the data to a computer in real time.

Several milling parameters were varied systematically in the multiwall carbon nanotube (MWCNTs) size reduction experiments. Changes were monitored by transmission electron microscopy (nanotube length distribution), Raman spectroscopy (characterization of defect sites) and nitrogen adsorption measurements. Results were compared to values obtained by using the Burgio-Rojac model of mechanical energy transfer.

Metal oxide nanoparticles were synthesized from their corresponding metal salts and $Na_2CO_3$ as precursors in NaCl as grinding medium (matrix). The prepared samples were calcined and washed with distilled water when necessary. Synthesized materials were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffractometry (XRD), Raman and Fourier transform infrared (FT-IR) spectroscopy, surface area and pore size determination by nitrogen adsorption, thermogravimetric analysis (TG), electron diffraction (ED) and energy-dispersive X-ray spectroscopy (EDS).

$TiO_2$ nanoparticles were synthesized from $TiCl_4$ and $Na_2CO_3$ in NaCl medium in a planetary ball mill. We prepared trititanates nanotubes (TiONT) and nanowires (TiONW) by the alkali hydrothermal method. Titanate nanowires were converted into TiONT and $TiO_2$ nanoparticles by a subsequent mechanical treatment in the mill.

## 2. New scientific results

### 1. Milling experiments on multiwall carbon nanotubes.

1.1. We verified that the Burgo-Rojac model of mechanical energy transfer is applicable to the planetary ball milling of nanomaterials. This model allows the calculation of the impact energy of a single ball hit event ($E_b$) as well as the amount of the total (cumulative) energy transferred to the milled material during the process ($E_{cum}$). By comparing results from a simple statistical model with those of the Burgio-Rojac model we were able to demonstrate that the latter provides a more appropriate framework for the interpretation of milling-induced changes in the length and quality of multiwall carbon nanotubes. The effects of the studied parameters (speed and duration of the milling, number and size of the balls used) were visualized on milling maps that revealed the following: (1) the energy necessary for fracturing a nanostructure can be made available by controlling $E_b$, (2) the size distribution of the product mixture can be tuned by changing $E_{cum}$ and (3) changing the diameter and the number of grinding balls has a pronounced effect on $E_b$ and $E_{cum}$, respectively. These two energy "types" are not fully interchangeable.

1.2. We were the first to quantitatively characterize certain structural changes experienced by multiwall carbon nanotubes during ball milling as functions of the operational parameters of the mill. Raman spectra were measured to evaluate the extent of milling-induced amorphization from the intensity ratio of the D and G lines. The $I_D/I_G$ ratio increased even at low $E_b$ due to the rapid accumulation of wall defects. Supplementary nitrogen adsorption measurements provided evidence for the $E_{cum}$ dependence of the pore volume increase and the specific surface area increase caused by the fracturing of nanotube ends.

### 2. Observations on the kinetics of mechanochemical reactions during the synthesis of metal-oxide nanoparticles.

We described and explained the anomalous behaviour of the pressure vs. time function recorded during the mechanochemical synthesis of metal oxide nanoparticle synthesis with $Na_2CO_3$ reactant. A combined XRD, FT-IR and TG investigation revealed that excess $Na_2CO_3$ can react with the generated $CO_2$ and moisture in the milling drum to yield

$NaHCO_3$. This phenomenon buffers the pressure increase that is due to the progression of the primary mechanochemical reaction, and this in turn could result in erroneous interpretation of reaction kinetic data based on pressure changes. Increasing the relative amount of $Na_2CO_3$ intensifies the phenomenon up to the point where all formed $CO_2$ is immobilized, therefore, the relationship between pressure and conversion in such systems is complex and nonlinear. If the metal-containing precursor salt and $Na_2CO_3$ are mixed in stoichiometric ratio then the $NaHCO_3$ formed in the first phase of the reaction can release $CO_2$ again in the second phase rapidly. The unexpected step observed in the pressure vs reaction time curve can be interpreted on this basis.

## 3. Mechanochemical synthesis of metal oxide nanoparticles.

3.1. Using a tin oxide nanoparticle model we proved that the planetary ball mill is well-suited for the fast, high-yield production of metal oxide nanoparticles from the corresponding metal salts and $Na_2CO_3$ in NaCl matrix. The latter plays a major role in the separation of the nanoparticles and in transferring the mechanical energy to the reactants. The synthesized metal oxide nanoparticles feature monodisperse size distribution (average diameter: 9 nm) and uniform morphology. The developed method was successfully applied in the synthesis of $SnO_2$, $MnO_2$, CdO, CoO, ZrO and ZnO nanoparticles.

3.2. The mechanochemical carbonate reaction route was adapted to the preparation of nickel-ferrite nanoparticles. We developed the first single-step mechanochemical procedure that yields $NiFe_3O_4$ nanoparticles with an average diameter of 8.5 nm. The in situ synthesis of high energy internedier ferrite-precursor oxides (NiO, $Fe_2O_3$) was identified as the key to the success of the new procedure.

## 4. Mechanochemically induced phase transformations in titanate structures.

4.1. $TiO_2$ nanoparticles with an average diameter of 7.2 nm were successfully synthesized by the mechanochemical carbonate route. We demonstrated that by changing the milling conditions it is possible to tune the synthesis towards either amorphous, anatase or rutile titania.

4.2. We provided the first experimental evidence for the possibility of transforming titanate nanowires into titanate nanotubes, even though the former are thermodynamically

favored over the latter. This was achieved by milling titanate nanotubes using small to medium milling energies and making use of the quenching of high energy transition states typical for mechanochemical processing. Prolonged high energy milling disintegrated titanate nanotubes into amorphous polymorphic $TiO_2$ nanoparticles.

## 4. Practical environmental scientific aspects of the results

I consider my doctoral work as fundamental research since my original goals did not include any practical applications. Nevertheless, it is possible to identify three outcomes that may have some applied environmental scientific relevance. They all originate from the fact that mechanochemistry offers simple, solvent-free and low capital investment (that is, sustainable and environmentally benign) synthetic routes for the industrial scale production of nanostructured materials.

- Milling maps can be used to synchronize milling conditions in different mills, and this may help in scaling up mechanochemical nanoparticle synthesis methods. Milling maps are derived from the Burgio-Rojac energy transfer model, which in turn was confirmed for nanomaterials by us.
- The actual conversion of a mechanochemical reaction involving a carbonate reaction partner in an industrial setting can be theoretically inferred from the pressure vs. time function. However, the nonlinearity of this function makes this a non-trivial task. Our interpretation of the pressure-related phenomena remedies this situation and renders the pressure function available for conversion calculation regardless of its complexity.
- The single step low temperature mechanochemical synthesis of rutile and nickel-ferrite nanoparticles at close to room temperature paves the way towards more energy efficient, greener production methods.

## 5. Publications related to the present thesis

1. **Spectroscopic studies on the formation kinetics of $SnO_2$ nanoparticles synthesized in a planetary ball mill**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   *Journal of Molecular Structure,* 2007, (834-836) pp. 430-434.
   IF: 1,78

2. **Effect of planetary ball milling process parameters on the nitrogen adsorption properties of multiwall carbon nanotubes**
   I.Z. Papp, **G. Kozma**, R. Puskás, T. Simon, Z. Kónya, Á. Kukovecz
   *Adsorption,* 2013, (2-4) pp. 687-694.
   IF: 1,85

3. **Non-equilibrium transformation of titanate nanowires to nanotubes upon mechanochemical activation**
   **G. Kozma**, Z. Kónya, Á. Kukovecz
   *RSC Advance*s, 2013, (21) pp. 7681-7683.
   IF: 3,907

4. **Experimental validation of the Burgio–Rojac model of planetary ball milling by the length control of multiwall carbon nanotubes**
   **G. Kozma**, R. Puskása, I.Z. Papp, P. Bélteky, Z. Kónya, Á. Kukovecz
   *Carbon*, 2016, (105), pp: 615-62
   IF: 6,89

5. **$CO_2$ capture in $NaHCO_3$ form explains the anomalous pressure evolution during the mechanochemical synthesis of $SnO_2$ nanoparticles**

## 6. Presentations and posters related to the present thesis

1. **Synthesis and characterization of tin-oxide nanoparticles**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   V. VMTDK, Serbia/Novi Sad, 2006. (presentation)
   VII. TMTDK, Romania/Timisoara, 2006. (presentation)

2. **Mechanochemical synthesized nanoparticles: Synthesis and characterization**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   ETDK, Romania/Cluj-Napoca, 2007. (presentation)

3. **Synthesis and characterization of Cr doped $SnO_2$ nanoparticals using mechanochemistry**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   The 7$^{th}$ Students' Meeting, Serbia/Novi Sad, 2007. (presentation)

4. **Spectroscopic characterization of mechanochemically synthesized Cr/SnOx nanocomposites**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   XXIX. EUCMOS, Croatia/Opatija, 2008. (presentation)

5. **2-Magnon Raman behavior of NiO nanoparticles**
   F. Shahzad, P. Knoll, K. Ettinger, K. Nadeem, H. Krenn, K. Pressl, P. Granitzer, Á. Kukovecz, **G. Kozma**, Z. Kónya,I. Letofsky-Papst
   22nd ICORS, USA/Boston, 2010. (abstract book)

6. **Mechanochemistry: Properties, synthesis and kinetic**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   NAPEP meeting, Finland/Oulu, 2012. (presentation)

7. **Observation of size determination of multiwalled carbon nanotubes and titanate nanowires in planetary ball mill by transmission electron microscopy**
   **G. Kozma**, Á. Kukovecz, Z. Kónya
   MMT, Hungary/Siófok, 2012. (presentation)

8. **Investigation of sorption properties of modified structure $TiO_2$ nanowires and nanotubes by planetary ball mill**
   **G. Kozma**, A. Sápi, Á. Kukovecz, Z. Kónya
   VIII. ISSHAC, Poland, Krakow, 2012. (presentation)

9. **Investigation of adsorption properties on different sized multiwall carbon nanotubes milled by planetary ball mill**
   Z. Papp, **G. Kozma**, A. Kukovecz, Z. Kónya
   VIII. ISSHAC, Poland, Krakow, 2012. (abstract book)

10. **Sorption properties of mechanical modified titanate nanowires and nanotubes**
    **G. Kozma**, A. Sápi, Á. Kukovecz,
    5$^{th}$ SIWAN, Szeged, 2012. (poster)

11. **Mechanokémiával előállítható nanoszerkezetek**
**G. Kozma**, A. Sápi, Á. Kukovecz, Z. Kónya
Anyagtudományi Kutatások Szegeden, Szeged, 2014. (presentation)

12. **Investigation of modified structure $TiO_2$ nanowires and nanotubes by planetary ball mill**
**G. Kozma**, A. Sápi, Á. Kukovecz, Z. Kónya
12th MCM, Hungary/Eger, 2015. (poster)

## 7. Other publications

1. **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
*Central European Journal of Occupational and Environmental M.,* 2008, (3) pp. 277-290
IF: 1,98

2. **Synthesis of Zinc Glycerolate Microstacks from a ZnO Nanorod Sacrificial Template**
R. Rémiás, Á. Kukovecz, M. Darányi, **G. Kozma**, S. Varga, Z. Kónya, I. Kiricsi
*Europian Journal of Inorganic Chemistry*, 2009 (24) pp. 3622-3627.
IF: 2,93

3. **Study of the parameters influencing the co-grinding process for the production of meloxicam nanoparticles**
L. Kürti, Á. Kukovecz, **G. Kozma**, R. Ambrus, M.A. Deli, P. Szabó-Révész
*Powder Technology,* 2011 (1) pp. 210-217.
IF: 2,437

4. **Nervous system effects of dissolved and nanoparticulate cadmium in rats in subacute exposure**
E. HorvátH, G. Oszlánczi, Zs. Máté, A. Szabó, **G. Kozma**, A. Sápi, Z. Kónya, E. Paulik, L. Nagymajtényi, A. Papp
*Journal of Applied Toxicology,* 2011,(5) pp. 471-476.
IF: 2,96

5. **Self-assembling of Z-alpha-pyridylcinnamic acid dimers over polycrystalline Ag and Au surfaces followed by FT-IR and atomic force microscopies**
K. Csankó, M. Darányi, **G. Kozma**, Á. Kukovecz, Z. Konya, P. Sipos, I. Palinkó
*Journal of Molecular Structure*, 2011, 993:(1-3) pp. 67-72.
IF: 1,585

6. **Consequences of subacute intratracheal exposure of rats to cadmium oxide nanoparticles: Electrophysiological and toxicological effects**
A. Papp, G. Oszlánczi, E. Horváth, E. Paulik, **G. Kozma**, A. Sápi, Z. Kónya, A. Szabó,
*Toxicology and Industrial Health*, 2012, (10) pp. 933-941.
IF: 1,66

7. **Self-assembling of 2,3-phenyl/thienyl-substituted acrylic acids over polycrystalline gold**
K. Csankó, **G. Kozma**, L. Valkai, Á. Kukovecz, Z. Kónya, P. Sipos, I. Palinkó
*Journal of Molecular Structure* 2013, (1044) pp. 32-38.
IF: 1,585

8. **Toxic metal immobilization in contaminated sediment using bentonite- and kaolinite-supported nano zero-valent iron**
   DV. Kerkez, DD. Tomašević, **G. Kozma**, BD. Dalmacija, MB. Dalmacija, MR. Bečelić-Tomin, Á. Kukovecz, Z. Kónya, S. Rončević
   *Journal of Nanoparticle Research*, 2014, (8) pp. 2548
   IF: 2,65

9. **Three different clay-supported nanoscale zero-valent iron materials for industrial azo dye degradation: A comparative study**
   DV. Kerkez, DD. Tomašević, **G. Kozma,** MR. Bečelić-Tomin, P. Miljana, SD Rončević, D. Srdjan, BD. Dalmacija, Á. Kukovecz, Z. Kónya
   *Journal of the Taiwan Institute of Chemical Engineers*, 2014, (5) pp. 2451-2461.
   IF: 2,655

10. **Environmentally benign synthesis methods of zero valent iron nanoparticles**
    **G. Kozma**, A. Rónavári, Z. Kónya, Á. Kukovecz
    *ACS Sustainable Chemistry & Engineering*, 2015, (1) pp. 291-297.
    IF: 4,64

11. **Development of Ibuprofen-loaded nanostructured lipid carrier based-gels: characterization and investigation of in vitro and in vivo penetration through the skin**
    B. Sütő, Sz. Berkó, **G. Kozma**, Á. Kukovecz, M. Budai-Szűcs, G. Erős, L. Kemény, A. Sztojkov-Ivanov, R. Gáspár, E. Csányi
    *International Journal of Nanomedicine*, 2016, (11) pp. 1201-1212.
    IF: 4,742

12. **Size-Dependent Toxicity Differences of Intratracheally Instilled Manganese Oxide Nanoparticles: Conclusions of a Subacute Animal Experiment**
    Zs. Máté, E. Horváth, **G. Kozma**, T. Simon, Z. Kónya,E. Paulik , A. Papp, A.Szabó
    *Biological Trace Element Research*, 2016, (1) pp. 156-166.
    IF: 1,70

13. **Multi-Walled Carbon Nanotubes: Chapter 5**
    Á. Kukovecz, **G. Kozma**, Z. Kónya
    *Springer Handbook of Nanomaterials,* 2013. pp. 147-188. (ISBN:978-3-642-20594-1)

14. **Nervous system and general toxic effects in rats after subacute intratracheal application of nanosized lead oxide**
    Oszlánczi G, Horváth E, Szabó A, Papp A, Pusztai P, Szabó M, **Kozma G**, Sápi A, Kónya Z, Vezér
    *Neuroforum*, 2011, (1) pp. T11-11B.
    IF: 0

15. **The effect of cadmium on behavioral and electrophysiological parameters of rats after subacute exposure in two different forms**
    Horváth E, Oszlánczi G, Máté Zs, Szabó A, Papp A, **Kozma G**, Sápi A, Kónya Z, Nagymajtényi
    *Neuroforum*, 2011, (1) pp. T13-6C.
    IF: 0

16. **Protective effect of green tea against neuro-functional alterations in rats treated with $MnO_2$ nanoparticles**
Sárközi K, Korosine E, Máté Zs, Papp A, **Kozma G**, Galbács G, Kalomista I.
*Journal of the Science of Food and Agriculture, 2016,*
IF: 2,076

## 8. Other presentations, posters and conference attendances

1. **An Atomic Force Microscopy study on the oligomerization behavior of beta-amyloid**
**G. Kozma**, L. Fülöp, Á. Kukovecz, Z. Kónya
MMT Hungary/Siófok, 2009. (presentation)

2. **Groundwater remediation using zero valent iron nanoparticles**
**G. Kozma**, Á. Kukovecz, Z. Kónya
16th DKMT, Hungary/Szeged, 2012 (presentation)

3. **Investigation of self-assemble β-amiloid Aβ(16–22), $CH_3CO$-KLVFFAE-$NH_2$ segment by more microscopic process**
**G. Kozma**, L. Fülöp, Á. Kukovecz, Z. Kónya
MMT, Hungary/Siófok, 2010. (presentation)

4. **Felszín alatti vizek kármentesítése nanoméretű vas segítségével**
**G. Kozma**, Á. Kukovecz, Z. Kónya
I. KKSZ, Hungary/Mátraháza, 2012 (presentation)

5. **Atomic Force Microscopic investigations on peptide aggregation and self-assembling peptide nanotubes**
**G. Kozma**, Á. Kukovecz, Z. Kónya
NAPEP meeting, Hungary/Szeged, 2012 (presentation)

6. **Talajvizek tisztítása nanovassal: egy sikeres k+f projekt bemutatása**
**G. Kozma**, Á. Kukovecz, Z. Kónya
II. KKSZ, Hungary/Dobogókő, 2013 (presentation)

7. **Hatóanyag és kármentesítési technológia fejlesztése klórozott alifás szénhidrogénekre**
**G. Kozma**, É. Benő, Á. Kukovecz, Z. Kónya,
KSZGYSZ-2013, Hungary/Budapest, 2013 (presentation)

8. **Groundwater remediation using zero valent iron nanoparticles**
**G. Kozma**, Á. Kukovecz, Z. Kónya
MATCROSS meeting, Serbia/Novi Sad, 2013 (presentation)

9. **Intellectual and industrial property in Hungary and in the EU**
**G. Kozma**, Á. Kukovecz, Z. Kónya
NAPEP meeting, Hungary/Szeged, 2013 (presentation)

10. **Microscopy education in Szeged at the Department of Applied and Environmental Chemistry**
**G. Kozma**, D. Madarász, Á. Kukovecz, Z. Kónya
MMT, Hungary/Siófok, 2014. (presentation)

11. **Nanorészecskék a környezetvédelemben: a laboratóriumtól a megvalósításig**
    **G. Kozma**, Á. Kukovecz, Z. Kónya
    AKKTB annual meeting, Hungary/Szeged, 2014 (presentation)

12. **Groundwater remediation using environemntally benign zero valent iron nanoparticles**
    **G. Kozma**, A. Rónvári, Á. Kukovecz, Z. Kónya
    IBSC-2016, Serbia /Novi Sad

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| Peer-reviewed papers total: 20 | out of this, related to the topic of thesis: 4 |
| Cumulative impact factor: 48.351 | out of this, related to the topic of thesis: 14.405 |
| Independent cites total: 89 | out of this, related to the topic of thesis: 16 |