Article

Journal of
Nanoscience and Nanotechnology
Vol. 18, 1–7, 2018
www.aspbs.com/jnn

Electron Microscopy Investigation of Coated Multiwall Carbon Nanotubes Prepared by Reactive Ball Milling

Judit Major[1], Jin Won Seo[2], Endre Horváth[3], Ákos Kukovecz[1], László Forró[3], and Klara Hernadi[1,*]

[1] *Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged, H-6720, Hungary*
[2] *Departement Metaalkunde en Toegepaste Materiaalkunde, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44 – Bus 2450, B-3001 Heverlee, Belgium*
[3] *Laboratory of Physics of Complex Matter (LPMC), Ecole Polytechnique Fédérale de Lausanne, Centre Est, Station 3, CH-1015, Lausanne, Switzerland*

Homogeneous and stable inorganic coating of SiO_2, Al_2O_3 and TiO_2 was obtained on the surface of multiwall carbon nanotubes (MWNTs) by mechanically mixing them with precursor compounds in a planetary ball mill and by subsequent hydrolysis. Detailed studies by means of transmission and scanning electron microscopy revealed that the milling time as well as the number of balls significantly affects the homogeneity of the layer formed. Our results demonstrate that planetary ball milling can be an effective and low-cost process for the production of homogenous coating of oxides on MWNTs in a large-scale.

Keywords: Carbon Nanotube, Composite, Oxide Coating, Ball Milling, Electron Microscopy.

1. INTRODUCTION

Carbon nanotube (CNT) based composite materials are currently one of the most promising applications of CNTs and have been investigated by many research groups. Due to the outstanding combinations of high-aspect ratio, low density, exceptional electrical, thermal and mechanical properties, CNTs have been considered as the ideal additive to advanced composite materials,[1–4] such as polymer composites, photocatalysts[5–7] or chemical sensors.[8,9]

In the last few years attachment of various inorganic compounds onto single-wall and multiple-wall CNTs has been achieved by several groups. For example, oxide nanoparticles such as silica,[10–13] tin oxide,[14] alumina,[15,16] zinc oxide[17] and titania[18,19] have been successfully deposited onto the surface of CNTs by impregnation technique, chemical solution route or hetero-coagulation method. The experiments performed by a sol–gel method using classical alkoxides as $Ti(OEt)_4$ and $Ti(OPri)_4$ and by hydrothermal hydrolysis of $TiOSO_4$ resulted in different TiO_2 morphologies.[20] With this technique nanotubes were coated either with a continuous TiO_2 thin film when the precursor was $Ti(OEt)_4$, or with TiO_2 nanoparticles when the precursor was $Ti(OPri)_4$. By hydrothermal treatment, more compact and crystalline nanocomposites could be obtained. Zhang et al. used $TiCl_4$ as starting material and presented a method for coating single walled CNTs by amine-terminated TiO_2 nanoparticles.[21]

The poor solubility of individual single-wall CNTs in solutions required for processing and the lack of specificity of titania formation exclusively at the surface of the single-wall CNTs called for further studies. It was demonstrated that a multifunctional peptide could suspend single-wall CNTs as individuals and precipitate silica or titania from water-soluble precursors at the surface of the nanotubes without covalent functionalization of the carbon nanotubes under mild conditions.[22] Chen et al. successfully applied the electroless deposition method for the coating of multiwall CNTs (MWNTs), which were shortened prior composite preparation by long-time mechanical grinding.[23]

Ball milling, also called mechanical alloying, is a simple and favorable technique for generation of equilibrium and non-equilibrium materials. It has been applied to CNTs for curving,[24] shortening,[25,26] to convert them into nanoparticles or nanoporous carbon[27,28] or to obtain a better distribution.[29] It has also been reported that hydrogen adsorption properties[30] as well as lithium intercalation properties[31] of CNTs can be improved. We used the planetary ball milling technique to produce a stable inorganic

*Author to whom correspondence should be addressed.

layer on the surface of MWNTs. Our results indicate that ball milling can be a simple and highly effective homogenizing method in order to obtain homogeneously covered MWNTs in large quantities and in a controllable way. This hybrid material can be used for further processing in various application fields such as (photo)catalysis, sensing, polymer reinforcement, etc.

The aim of the present work to produce homogeneously covered CNT without separated inorganic particles using a simple, cheap, one step method in a planetary ball mill. These multi-walled carbon nanotube-based composites are promising candidates as thick film gas sensors or catalysts.

2. EXPERIMENTAL DETAILS

2.1. Materials

—MWNTs were prepared by the decomposition of acetylene (CVD method) in a rotary oven at 720 °C using Fe, $Co/CaCO_3$ catalyst.[32] SEM image of the purified MWNT sample is shown in Figure 1.
—Titanium (IV) ethoxide (TEOTi)
—Tetraethyl orthosilicate (TEOS)
—Aluminium isopropoxide (AlIP)
—Distilled water.

All chemicals were purchased from Sigma-Aldrich Co.

2.2. Planetary Ball Mill

A Pulverisette 6 type planetary ball mill, equipped with a 250 ml grinding bowl and stainless steel balls of 10 mm size was used for homogenization. The rotational speed was varied from 100 to 400 rpm. The respective treatment times of planetary ball milling were 10 to 120 minutes.

2.3. Sample Preparation

Purified MWNTs were dried in an oven at 100 °C for 60 min. Approx. 0.1 g was weighed for further experiments. The amount of precursor material was estimated as follows: specific surface area of MWNT is approx. 400 m^2g^{-1} so the surface of our sample to be covered is about 50 m^2.[33] From the radii of metal atoms of precursor materials, the estimated volume of metal oxide can be calculated. From these data—possessing parameters of compounds—the approximate amount of precursor required can be determined. Taking into account some unavoidable hydrolysis and loss on the walls, this calculated value was increased by 20%. Thus for 0.1 g MWNT 1.5 mL liquid precursor (TEOTi and TEOS) or 2.0 g AlIP was added which was homogenized in the ball mill under conditions described hereafter. Since the equipment is not suitable for providing an inert atmosphere, the latter step was done as quickly as possible then the grinding bowl was closed. Hereby hydrolysis caused by humidity could be minimized.

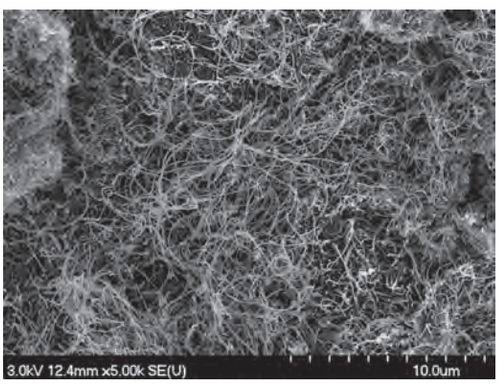

Figure 1. SEM image of the purified MWNT sample produced by CVD method.[39]

In this study the effect of milling time, number of balls and rotation per minute on the quality were investigated. The milling time was varied mostly in the range of 10 to 120 minutes. During preliminary measurements, however, lower milling times were also applied. While the number of balls was 10, 20 or 30, the rotation per minute was changed from 100 to 400. The experiments were carried out in a planetary ball mill and we want to emphasize here that the main goal of this work was homogenization and not real grinding.

After homogenization a few drops of distilled water were added in order to hydrolyze precursor molecules and to form their oxides/hydroxides.[12] Then samples were dried at 100 °C for 45 minutes.

2.4. Electron Microscopy

For qualitative characterization, products were investigated by transmission electron microscopy (TEM, Philips CM10), in particular, to verify the formation of inorganic coverage on the surface of MWNT. In order to observe representative portions, for normal resolution the TEM sample preparation involved grinding the material mechanically and gluing the ground powder on a Cu TEM-grid. High resolution transmission electronmicroscopy (HRTEM) characterization was carried out using a Philips CM300 FEG microscope operating at 300 kV. For HRTEM sample preparation, samples were dispersed in isopropanol and sonicated for 5 min. A droplet of suspension was put on a Cu TEM grid with a holey C film. (It is important to mention here that with this method a slight possibility of the sedimentation of thickly covered nanotubes occurs).

The observation of inorganic layer by normal resolution TEM is not always obvious, especially if the sample is homogeneous. During investigation the following direct or indirect proofs were searched: bare ends of MWNT peeping out from below the layer (generally marked with arrow in the figures); the contrast of the inner core of MWNT is significantly lower when covered; the surface of composite material is less smooth. High resolution investigation provided further evidence.

Scanning electron microscopy (SEM) was done on a Hitachi S-4700 Type II FE-SEM operating in the 5–15 kV range using a cold field emission gun. The samples were mounted on conductive carbon tape and sputter coated by a 5 nm thick Au/Pd layer in Ar atmosphere prior to the measurement.

3. RESULTS AND DISCUSSION

3.1. Effect of Ball Milling to Carbon Nanotubes

As already reported in the literature, ball milling can cause severe structural damages, in particular when high-impact milling and long milling time are applied.[34] Low-impact milling has revealed that the nanotubes length and their entanglement can be reduced in particular with increasing milling time, but the carbon nanotubes (CNTs) wall structure remained intact.[35] Planetary ball mill has the advantage that it generates tangential mechanical strain as the result of the ball rolling over the walls of the grinding container. Thus, only a small amount of mechanical energy is directly transferred to CNTs compared to for instance vibrating apparatus. Consequently, the milling procedure can be tuned to very soft, low-impact conditions. As the aim of our study was to produce a stable inorganic layer on the surface of MWNT, at first the optimum grinding parameters had to be found so that homogeneous distribution as well as effective interaction with the precursors can be obtained without any structural collapse of carbon nanotubes. Therefore, we studied at first multiwall carbon nanotubes without any precursor material after ball milling at different conditions. As previously reported by Kim et al.[26] carbon nanotubes milled for less than 5 hours (under comparable milling conditions) rather disentangle than undergo a structural transition. Raman scattering confirmed that there is a small increase in the defect density, but overall, there is no big difference in the microstructure for the milled samples. This is in agreement with our observation: ball milling even for several hours kept the carbon nanotubes structure unchanged in the case of well-chosen conditions. For testing the stability of the original sample, we loaded MWNT without Ti-compound and used the most drastic condition set: highest milling time, highest rpm and the maximum number of balls. After that we checked the quality by TEM. Based on TEM observations we assume that the generated defects are mainly located on the surface of carbon nanotubes and will promote the direct chemical bonding with the precursor molecules. However, as an increased milling time can result in cleavage or structural collapse,[36] the milling time was strictly limited to maximum 120 minutes.

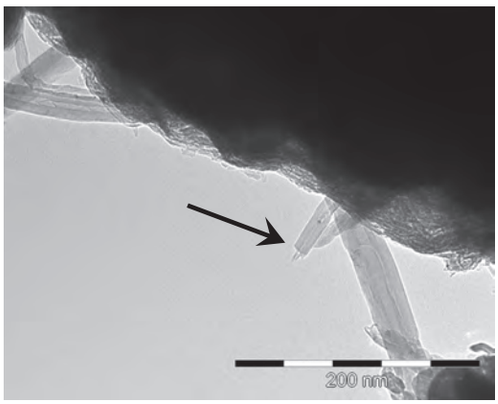

Figure 3. Representative TEM image of composite material prepared from AlIP: Al_2O_3/MWNT (240 min, 10 balls, 100 min^{-1}).

3.2. Effect of Ball Milling with Different Precursors

Grinding with precursor compounds such as Tetraethyl orthosilicate (TEOS), aluminium isopropoxide (AlIP) and titanium (IV) ethoxide (TEOTi) showed that ball-milling times below 10 minutes generally did not result in homogenous coverage. TEM studies indicated that the samples typically contained uncovered MWNTs and separated large inorganic particles. Figure 2 presents the

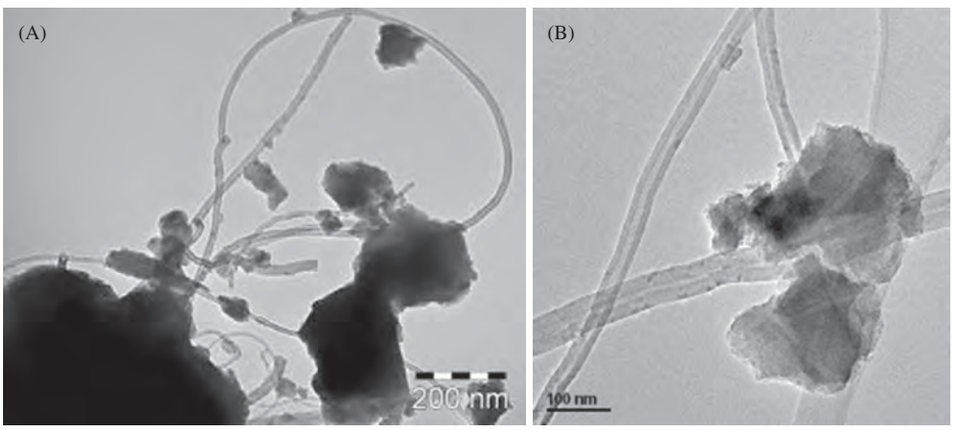

Figure 2. Composite material prepared from TEOTi with grinding parameters of 16 min, 10 balls, 100 min^{-1}: Images of (A) normal and (B) high resolution.

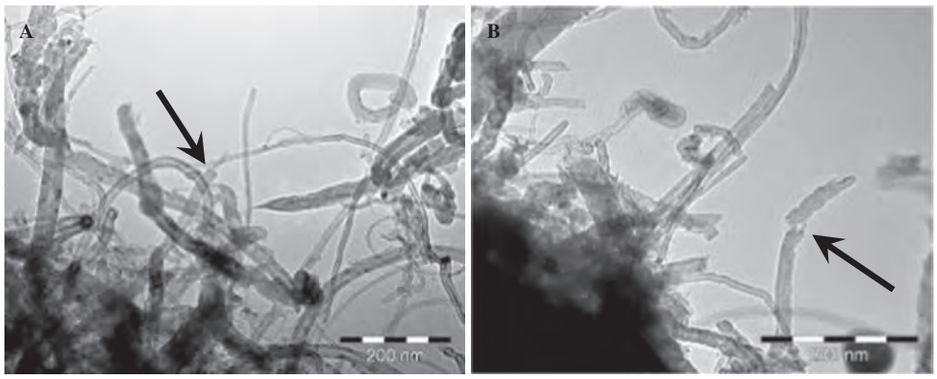

Figure 4. TEM images of composite material prepared from TEOS with different grinding parameters (A) 30 min, 10 balls, 100 min^{-1} (B) 120 min, 20 balls, 100 min^{-1}.

sample grinded with TEOTi precursor, where the carbon nanotubes are predominantly uncovered and separated from large titania particles even after 16 minutes of milling. When preparing alumina layers from AlIP precursor, rudimental coverage could be observed already after ten minutes of ball milling. Figure 3 shows sample prepared by milling AlIP precursor with MWNTs using 240 min milling time, 10 balls, and 100 min^{-1} rpm. However, segregated inorganic particles can be observed, TEM images proved that MWCNTs are also thickly covered. Results obtained with AlIP precursor also illustrate that increasing both the number of balls and milling time give rise to increased coverage of the sample whereas changing the speed of the rotation did not lead to a significant change in the characteristics of the product.

The observations with TEOS precursor were similar, however, at least 30 minutes were necessary for the formation of a coating. Increasing the number of balls and the milling time were again both favorable for the coverage of the final product. Besides bare carbon nanotubes,

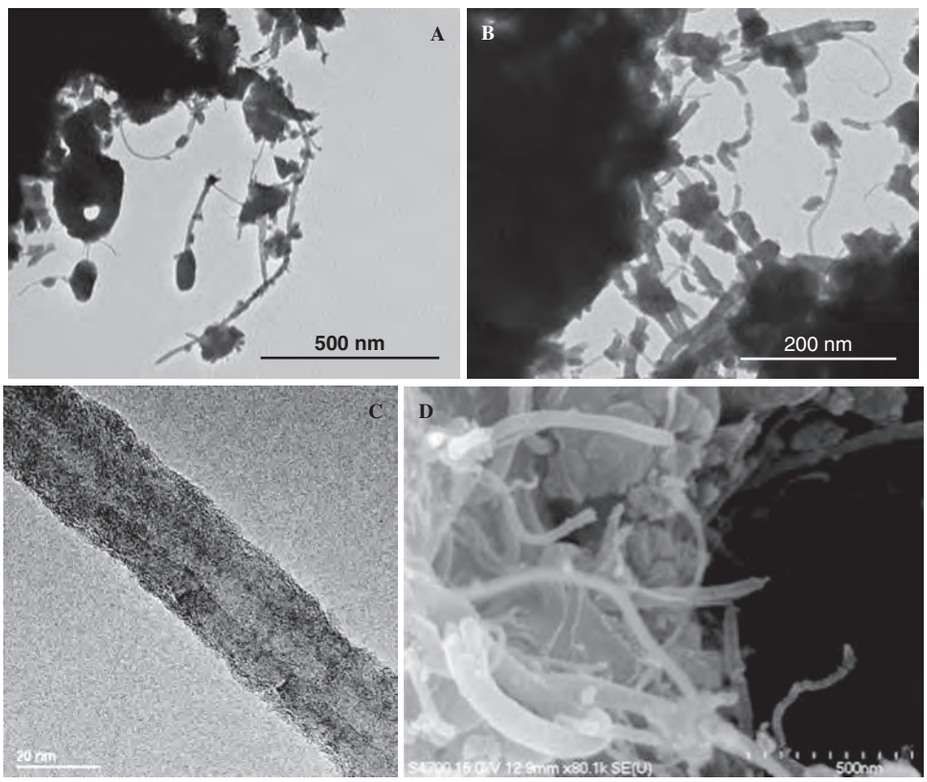

Figure 5. TEM images of composite material prepared from TEOTi with different milling times (A) 60 min, 10 balls, 100 min^{-1} (B) 120 min, 10 balls, 100 min^{-1} (C) 240 min, 10 balls, 100 min^{-1} (HRTEM) (D) SEM image.

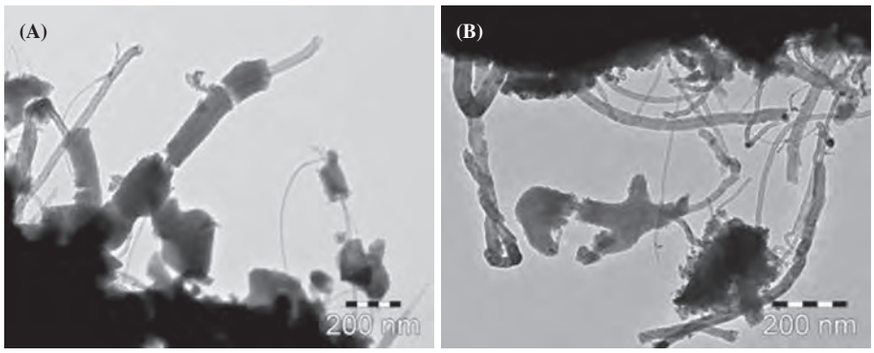

Figure 6. TEM images of composite material prepared from TEOTi with different milling times (A) 120 min, 20 balls, 100 min^{-1} (B) 120 min, 30 balls, 100 min^{-1}.

a few coated MWNT were found after 30 minutes by TEM investigation as it can be seen in Figure 4(A). The arrow in the image indicates one of the nanotubes coated with silica. The major part of carbon nanotubes was homogeneously covered with the inorganic material (see Fig. 4(B)) after 120 minutes of milling.

During the ball milling process, MWNTs and precursor material are periodically trapped between colliding balls and the container walls. In the case of AlIP, the precursor is solid in contrast to the other liquid precursors. Ahn et al. reported that dry-milling is more efficient and results in a more rapid collapse of CNTs compared to wet-milling.[36] They also demonstrated the difference in structural changes caused by both milling techniques: carbon nanotubes after dry and wet ball-milling were impregnated in a $SnCl_2$ dissolved HCl solution. SnO_2 nanoparticles formed after heating to 600 °C were covering the CNT surface for the dry-milled CNTs whereas the wet milled CNTs contained the particles inside the CNT hollow core. This result proves that dry-milling is more efficient in generating structural defects on the CNT surface and leads to a high defect density due to the higher number of impact. In addition, while milling with AlIP, the small particles produced during ball milling can be considered as many tiny balls, which cause additional high frequency impact as well as direct friction on the nanotubes. Therefore the required minimum milling time to obtain a coverage on CNTs is significantly lower for AlIP compared with the liquid precursors TEOTi and TEOS.

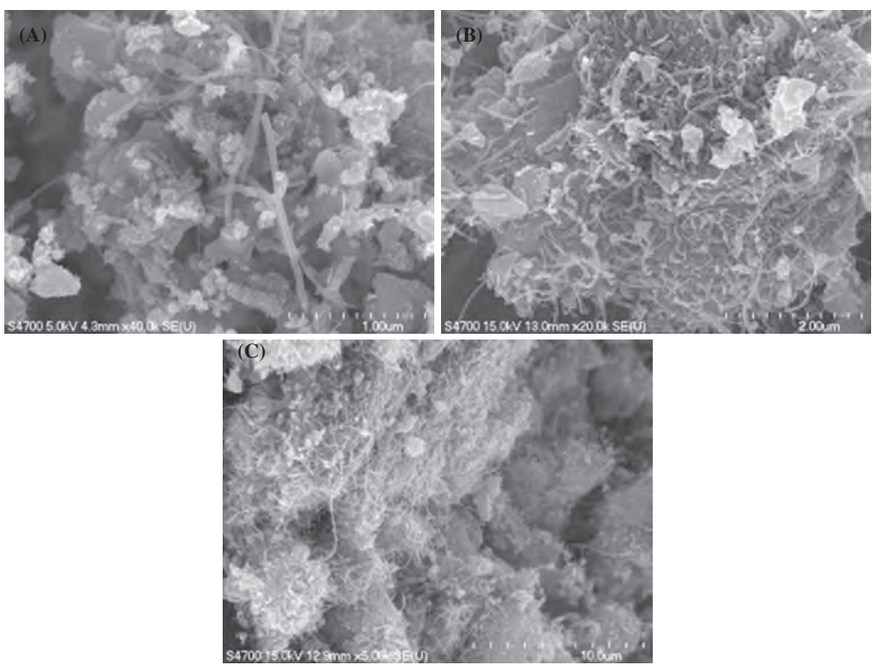

Figure 7. SEM images of TiO_2/MWNT samples prepared by various precursor-nanotubes ratio. (A) 1.5 mL TEOTi-100 mg MWNT; (B) 1.0 mL TEOTi-100 mg MWNT; (C) 0.5 mL TEOTi-100 mg MWNT.

3.3. Effect of Milling Time

Our preliminary investigations revealed that milling parameters might have a significant effect on the covering process. Therefore, all precursor materials have been investigated as a function of the milling time. As the general trend—longer milling time leads to better coverage—is very similar for all precursors, so we only present the results of TEOTi. Figures 5(A) and (B) show representative TEM images of composite materials obtained after 60 and 120 minutes of milling while keeping the number of balls and rotation speed constant. Whereas only rudiments of coverage can be observed after 60 minutes, the majority of the carbon nanotubes appear well-coated after 120 minutes. High resolution TEM investigations revealed that after 240 minutes MWNTs are homogeneously covered by an amorphous layer of titania (Fig. 5(C)). Imaging with SEM confirms that the homogeneous coverage was obtained on the macroscopic scale: Figure 5(D) shows a SEM image of perfectly covered carbon. Increasing the number of balls also increased the efficiency of the layer formation, whereas the speed of rotation did not have a significant effect on the process. Our preliminary results also indicate that the layer thickness increases with increasing number of balls (Figs. 6(A and B)).

Typically, when using the solvent-free method for the preparation of CNTs based composite materials, the amount of separated inorganic particles not reacting with CNTs cannot be controlled.[37] Consequently, the major part of the sample is contaminated with significant amount of various oxide side-products. By ball-milling, these supplementary particles can be avoided by adjusting the ration between the CNTs and the amount of added precursor. As described in the Experimental section, the quantity of the required precursor in order to cover the surface of carbon nanotubes was roughly estimated in a primitive calculation. SEM images presented in Figure 7 illustrate the samples prepared using 240 minutes milling time, 10 balls and 100 min^{-1} rotation speed and by adding 1.5, 1.0 and 0.5 mL of TEOTi, respectively. From these images it obvious that the amount of segregated titania particles is decreasing in the series until finally the sample with the lowest ratio contains almost no separated material. While the sample prepared with high TEOTi/MWNT ratio contains a significant amount of segregated titania particles, the composite material with the lowest TEOTi/MWNT ratio features a high density of homogeneously covered MWNTs in the macroscopic scale.

3.4. Investigation of the Stability of Composite Materials

For further potential applications, it is a key indicator whether the as-prepared samples are stable enough for future manipulation. In order to get information about the stability of well-covered composite material, a representative sample prepared by ball milling (240 min, 10 balls, 100 min^{-1}) was exposed to an intense grinding in an achat mortar for 15 minutes. Repeated TEM investigations revealed that the inorganic layer suffered no observable damage at all (Fig. 8). CNT prepared via CVD technique always contains surface OH groups which are able to seed layer formation.[12] In case of reactive ball milling their amount can be even higher.[34] Former investigations revealed that similar nanocomposites with CNT contain very strong covalent bond[38] thus provide proper stability of such nanocomposites, independently of the chemical nature of the coverage.

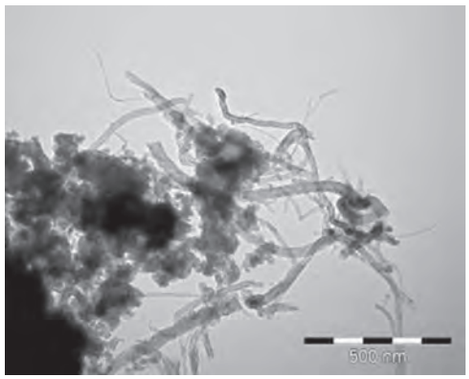

Figure 8. TEM image of a TiO_2/MWNT sample after intense grinding in a mortar.

4. CONCLUSION

In this paper we presented a novel, successful and cheap method for the preparation of MWNT-based inorganic composite materials. The planetary ball mill is a rather efficient tool not only for batchwise fine grinding down to colloidal fineness of hard to soft materials, dry or in suspension, but for the mixing and homogenization of emulsions and pastes, as well. Previous studies,[19] however, drew our attention to the possible damaging of MWNTs during ball-milling. According to our findings this problem can be avoided by the application of good quality CVD carbon nanotube samples. All three precursors (titanium (IV) ethoxide, tetraethyl orthosilicate, aluminium isopropoxide) tested in our investigations were suitable under certain milling conditions for the formation of a homogeneous coating (titania, silica, alumina) on the surface of MWNTs. For further application either on the field of catalysis or sensing, the suitability of as-produced composite material is of great importance. A stability assay proved that our samples are ready for further manipulation. This strength could originate both from the clean surface of MWNTs and from the character of CVD samples containing significant amount of defect sites, which may play a role in the firm binding of the layer. The optimization of precursor to MWNT ratio has been also done in order to avoid additional undesirable inorganic particles.

Acknowledgment: The authors are very grateful to the financial support provided by the OTKA NN114463 and K112531. This work was also supported by the Swiss National Science Foundation (No. 513733). Ákos Kukovecz and Klara Hernadi acknowledge the financial support of GINOP-2.3.2-15-2016-00013 project.

References and Notes

1. P. J. F. Harris, Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century, Cambridge University Press (**1999**).
2. M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, Carbon Nanotubes: Synthesis, Structure, Properties and Applications, Springer, Berlin (**2001**).
3. K. Nemeth, L. Kovacs, B. Reti, K. Belina, and K. Hernadi, *J. Nanosci. Nanotechnol.* 17, 5445 (**2017**).
4. J. W. Seo, E. Couteau, P. Umek, K. Hernadi, P. Marcoux, B. Lukic, C. Miko, M. Milas, R. Gaal, and L. Forro, *New J. Phys.* 5, 22 (**2003**).
5. B. Reti, Z. Major, D. Szarka, T. Boldizsar, E. Horvath, A. Magrez, L. Forro, A. Dombi, and K. Hernadi, *J. Mol. Catal. A-Chem.* 414, 140 (**2016**).
6. B. Reti, K. Mogyorosi, A. Dombi, and K. Hernadi, *Appl. Catal. A-Gen.* 469, 153 (**2014**).
7. S. Zaman, K. Zhang, A. Karim, J. G. Xin, T. Sun, and J. R. Gong, *Diam. Relat. Mat.* 76, 177 (**2017**).
8. Y. L. Liu, H. F. Yang, Y. Yang, Z. M. Liu, G. L. Shen, and R. Q. Yu, *Thin Solid Films* 497, 355 (**2006**).
9. M. T. Humayun, R. Divan, Y. Z. Liu, L. Gundel, P. A. Solomon, and I. Paprotny, *J. Vac. Sci. Technol. A* 34, 7 (**2016**).
10. Q. Fu, C. G. Lu, and J. Liu, *Nano Lett.* 2, 329 (**2002**).
11. Z. Li, S. G. Bi, B. C. Thompson, R. T. Li, and K. A. Khor, *Ceram. Int.* 43, 16084 (**2017**).
12. K. Hernadi, E. Ljubovic, J. W. Seo, and L. Forro, *Acta Mater.* 51, 1447 (**2003**).
13. E. A. Whitsitt and A. R. Barron, *Nano Lett.* 3, 775 (**2003**).
14. W. Q. Han and A. Zettl, *Nano Lett.* 3, 681 (**2003**).
15. K. Hernadi, E. Couteau, J. W. Seo, and L. Forro, *Langmuir* 19, 7026 (**2003**).
16. Ihsanullah, H. A. Asmaly, T. A. Saleh, T. Laoui, V. K. Gupta, and M. A. Atieh, *J. Mol. Liq.* 206, 176 (**2015**).
17. N. D. Alharbi, M. S. Ansari, N. Salah, S. A. Khayyat, and Z. H. Khan, *J. Nanosci. Nanotechnol.* 16, 439 (**2016**).
18. J. Sun and L. Gao, *Carbon* 41, 1063 (**2003**).
19. S. W. Lee and W. M. Sigmund, *Chem. Commun.* 780 (**2003**).
20. A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Beguin, and S. Bonnamy, *Carbon* 42, 1147 (**2004**).
21. J. Sun, M. Iwasa, L. Gao, and Q. H. Zhang, *Carbon* 42, 895 (**2004**).
22. M. J. Pender, L. A. Sowards, J. D. Hartgerink, M. O. Stone, and R. R. Naik, *Nano Lett.* 6, 40 (**2006**).
23. C. S. Chen, X. H. Chen, Z. Yang, W. H. Li, L. S. Xu, and B. Yi, *Diam. Relat. Mat.* 15, 151 (**2006**).
24. J. Y. Huang, H. Yasuda, and H. Mori, *Chem. Phys. Lett.* 303, 130 (**1999**).
25. N. Pierard, A. Fonseca, Z. Konya, I. Willems, G. Van Tendeloo, and J. B. Nagy, *Chem. Phys. Lett.* 335, 1 (**2001**).
26. Y. A. Kim, T. Hayashi, Y. Fukai, M. Endo, T. Yanagisawa, and M. S. Dresselhaus, *Chem. Phys. Lett.* 355, 279 (**2002**).
27. Y. Chen, J. D. Fitz Gerald, L. T. Chadderton, and L. Chaffron, *Appl. Phys. Lett.* 74, 2782 (**1999**).
28. Y. B. Li, B. Q. Wei, J. Liang, Q. Yu, and D. H. Wu, *Carbon* 37, 493 (**1999**).
29. K. Morsi and A. Esawi, *J. Mater. Sci.* 42, 4954 (**2007**).
30. F. Liu, X. B. Zhang, J. P. Cheng, J. P. Tu, F. Z. Kong, W. Z. Huang, and C. P. Chen, *Carbon* 41, 2527 (**2003**).
31. B. Gao, C. Bower, J. D. Lorentzen, L. Fleming, A. Kleinhammes, X. P. Tang, L. E. McNeil, Y. Wu, and O. Zhou, *Chem. Phys. Lett.* 327, 69 (**2000**).
32. E. Couteau, K. Hernadi, J. W. Seo, L. Thien-Nga, C. Miko, R. Gaal, and L. Forro, *Chem. Phys. Lett.* 378, 9 (**2003**).
33. K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, A. Fudala, and A. A. Lucas, *Zeolites* 17, 416 (**1996**).
34. Z. Konya, J. Zhu, K. Niesz, D. Mehn, and I. Kiricsi, *Carbon* 42, 2001 (**2004**).
35. A. Kukovecz, T. Kanyo, Z. Konya, and I. Kiricsi, *Carbon* 43, 994 (**2005**).
36. J. H. Ahn, H. S. Shin, Y. J. Kim, and H. Chung, *J. Alloys Compd.* 434, 428 (**2007**).
37. Z. Nemeth, B. Reti, Z. Pallai, P. Berki, J. Major, E. Horvath, A. Magrez, L. Forro, and K. Hernadi, *Phys. Status Solidi B-Basic Solid State Phys.* 251, 2360 (**2014**).
38. P. Berki, Z. Nemeth, B. Reti, O. Berkesi, A. Magrez, V. Aroutiounian, L. Forro, and K. Hernadi, *Carbon* 60, 266 (**2013**).

Received: 26 September 2017. Accepted: 5 January 2018.