

# Spider silk as a template for obtaining magnesium oxide and magnesium hydroxide fibers

Svetlana Dmitrović<sup>1</sup>, Marija Prekajski<sup>1</sup>, Bojan Jokić<sup>2</sup>, Goran Branković<sup>3</sup>, Aleksandra Zarubica<sup>4</sup>, Vladimir Žikić<sup>4</sup>, Branko Matović<sup>1</sup>

<sup>1</sup>Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

<sup>2</sup>Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

<sup>3</sup>Institute for Multidisciplinary Research, Department of Material Science, University of Belgrade, Belgrade, Serbia

<sup>4</sup>Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Niš, Serbia

## Abstract

Spider silk fibers, collected from *Pholcus Phalangioides* spider were used as a template for obtaining magnesium oxide (MgO, periclase) as well as magnesium hydroxide (Mg(OH)<sub>2</sub>, brucite) fibers. Magnesium oxide fibers were obtained in a simple manner by heat induced decomposition of magnesium salt (MgCl<sub>2</sub>) in the presence of the spider silk fibers, while magnesium hydroxide fibers were synthesized by hydration of MgO fibers at 50, 70 and 90 °C, for 48 and 96 h. According to Scanning electron microscopy (SEM), dimensions of spider silk fibers determined the dimension of synthesized MgO fibers, while for Mg(OH)<sub>2</sub> fibers, the average diameter was increased with prolonging the hydration period. The surface of Mg(OH)<sub>2</sub> fibers was noticed to be covered with brucite in a form of plates. X-Ray diffraction (XRD) analysis showed that MgO fibers were single-phased (the pure magnesium oxide fibers were obtained), while Mg(OH)<sub>2</sub> fibers were two- or single-phased brucite depending on incubation period, and/or incubation temperature.

**Keywords:** brucite, periclase, fibers, spider silk.

Available online at the Journal website: <http://www.ache.org.rs/HI/>

Magnesium oxide and magnesium hydroxide are very interesting materials that find application in many fields. Magnesium oxide (MgO, periclase or magnesia) is an inorganic compound that has been utilized in catalysis [1–5], toxic waste remediation [6], as a reinforcing agent [7], an additional component in refractory, paint and superconductor products industries [8,9], etc. It possess good buffering activity, heat resistance, insulating property and thermal conductivity [10]. MgO fibers are materials of special interest that possess high melting point (2800 °C), which makes them suitable for insulation applications [11]. MgO fibers have been synthesized by different techniques such as sol–gel, vapor deposition, electrospinning [11–13], yet no obtaining MgO fibers by natural fiber as a template has been reported in literature.

Magnesium hydroxide (Mg(OH)<sub>2</sub>, brucite) is a hydration product of magnesia that has been used in paper and pharmaceutical industry as well as for treatment of wastewater [14]. Magnesium hydroxide powders are recognized as potent flame retardant and smoke-suppressing additive in polymer production [15,16]. Preparation of magnesium hydroxide with specified mor-

phology, size and crystal structure is very important for different industrial purposes, especially due to its application at high loadings in production of retardant fillers. Different approaches have been used for preparing different shapes of magnesium hydroxide including needle-, wire-, rod-, -flower and lamellar-like Mg(OH)<sub>2</sub> by various techniques like hydrothermal, sol–gel, wet precipitation or electrochemical synthesis [17–23]. By reviewing the literature, no data for obtaining Mg(OH)<sub>2</sub> fibers was found.

Spider silk (SS) is famous by its excellent mechanical properties, but its utilization has been limited due to impossibility of farming cannibalistic spiders on industrial levels. With development of recombinant replication techniques, obtaining spider silk fibers in higher amounts became possible [24]. Today, spider silk has been introduced as a template for various applications [25–27], but, to our knowledge, it was not used as a template for production of magnesium oxide or hydroxide structures.

By using a very simple and cost effective method of decomposition magnesium chloride salt (MgCl<sub>2</sub>) in the presence of spider silk, we easily obtained MgO fibers. Spider silk dimensions determined the diameter and length of magnesia fibers, and hydration of these fibers resulted in formation of magnesium hydroxide fibers.

SCIENTIFIC PAPER

UDC 549.522:546.46:543

*Hem. Ind.* **72** (1) 23–28 (2018)

Correspondence: S. Dmitrović, Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11000 Belgrade, Serbia.

E-mail: [svetlana8@vinca.rs](mailto:svetlana8@vinca.rs)

Paper received: 04 April 2017

Paper accepted: 03 November 2017

<https://doi.org/10.2298/HEMIND170404018D>

## EXPERIMENTAL

Spider silk of *Pholcus phalangioides* spider was carefully collected from clean, dust free environment. Prior analysis, the silk was cleaned with isopropyl alcohol and subsequently thoroughly washed with water in order to remove the potential dust. The average diameter of the fiber was 200 nm.

The starting material for magnesia synthesis was magnesium chloride ( $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ , Sigma–Aldrich, 99.0%). First, 12 mg of spider silk mesh was immersed in 100 mL of 3 mol/L magnesium chloride solution. After ten minutes, the spider silk was removed from the solution, washed with distilled water and left to dry in the oven at 70 °C. As-obtained sample was subsequently calcined in air for 2 h in a furnace under the temperature of 600 °C, at the heating rate of 1 °C/min, and then left to cool in the furnace. This process yielded magnesium oxide fibers. Subsequently, MgO fibers were put in the coagulation bath at three different temperatures: 50, 70 and 90 °C, for 48 or 96 h in order to follow hydration of MgO and formation of  $\text{Mg}(\text{OH})_2$  crystals. The obtained samples were labeled according to the temperature and time in the bath as: fiber:50/48h, fiber:50/96h, fiber:70/48h, fiber:70/96h, fiber:90/48h and fiber:90/96h, respectively.

As synthesized samples were characterized by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) measurements.

The phase composition of samples was examined by X-ray diffraction (Rigaku Ultima IV, Japan). The X-ray beam was nickel-filtered  $\text{CuK}\alpha 1$  radiation ( $\lambda = 0.1540$  nm, operating at 40 kV and 40 mA). XRD data were collected from 10 to 80° ( $2\theta$ ) at a scanning rate of 5°/min. Phase analysis was done by using the PDXL2 software (version 2.0.3.0, 2011, Rigaku Corporation, Tokyo, Japan), with reference to the patterns of the International Centre for Diffraction Data base (ICDD), version 2012.

Morphology of MgO fibers was studied by field emission scanning electron microscopy (FESEM) TESCAN Mira3 XMU (Czech Republic) at 20 kV, while morphology of  $\text{Mg}(\text{OH})_2$  fibers was examined by using scanning electron microscope (SEM, TESCAN Vega TS 5130 MM, Czech Republic).

## RESULTS AND DISCUSSION

Figure 1 shows the FESEM image of the product that was obtained after heating SS previously immersed in  $\text{MgCl}_2$  solution at 600 °C for 2 h. It is well known that the temperature of calcination affects MgO properties [28]. Magnesium oxide obtained at lower temperatures (600 °C) hydrates at a greater extent than the one synthesized at higher temperatures [29], so the calcination temperature of 600 °C has been

chosen for obtaining MgO. It can be seen that fiber-like structures were obtained. Dimensions of the MgO fibers were determined by length and the diameter of spider silk fibers. Thus the average diameter of MgO fibers was 200 nm. By the time reaching the temperature of 600 °C in the furnace, all the organic compounds in spider silk decomposed to carbon dioxide and water releasing magnesium oxide in a form of fibers. Under the specified conditions, the following reaction occurred:

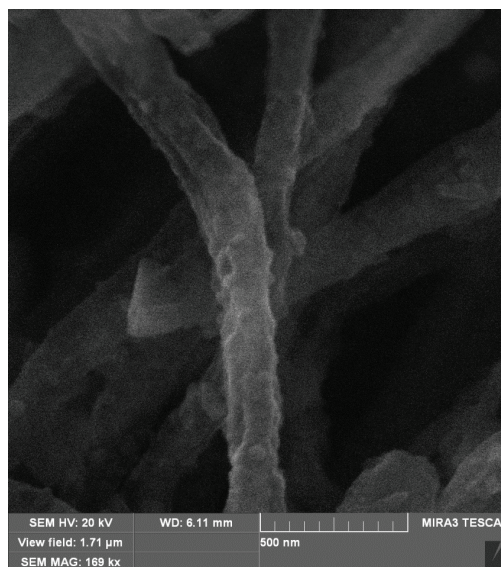
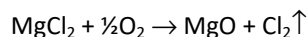
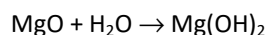


Figure 1. FESEM image of MgO fibers obtained via using spider silk as a template.

Hydrating magnesia is a common process for obtaining  $\text{Mg}(\text{OH})_2$ , and hydration conditions are of special importance for designing  $\text{Mg}(\text{OH})_2$  with desired morphology and properties [14]. In order to follow hydration of MgO fibers, as-obtained fibers were incubated in the water bath at three different temperatures: 50, 70 and 90 °C for 48 and 96 h. The process was described by the reaction:



Figures 2a and b present SEM images of fibers obtained after MgO hydration in coagulation bath at 50 °C after 48 (fiber:50/48h) and 96 h (fiber:50/96h), respectively. The diameter of the hydrated fibers is noted to be increased, and was between 1 and 2 μm for fiber:50/48h, and >2 μm for fiber:50/96h. Increasing the diameter of fibers is a result of fast and intensive growth of plate like brucite crystals along the fibers. It could be seen that formed brucite crystals on the surface of the fibers were in a form of plates, physically inseparable as a result of simultaneous growth from agglomerated grains [30]. Formation of this type of

plates is typical for brucite and is correlated with its crystallographic structure [19].

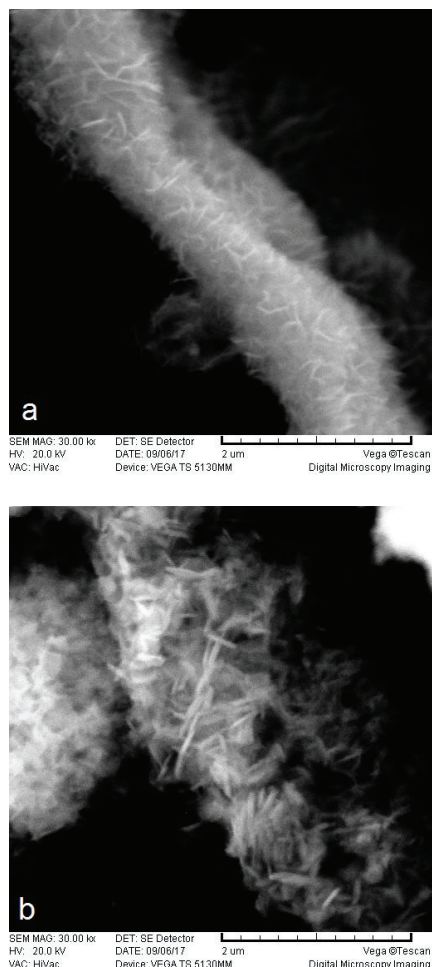


Figure 2. SEM micrographs of fibers obtained in coagulation bath at 50 °C: a) fiber: 50/48 and b) fiber:50/96h.

With increasing hydration temperature crystallization capability was increased, as expected and previously reported [30]. At temperature of 70 °C, after 48 h of incubation (fiber:70/48h) the average diameter was estimated to be 6–7 µm (Fig. 3a), while for the longer incubation period (fiber:70/96h) the diameter was even higher (>15 µm, Fig. 3b).

Incubation at temperature of 90 °C resulted in aggregated inseparable fibers (fiber:90/48h) (Fig. 4), and with prolonging the procedure to 96 h, the growth of brucite crystals was so fast and intensive, followed by aggregation of Mg(OH)<sub>2</sub> crystals, that no fibers could be detected.

The XRD patterns of the attained samples are presented in Figure 5. The lowest positioned pattern presents XRD results of MgO fibers and corresponds to diffraction peaks of a periclase (JCPDS 4-829). Characteristic peaks corresponding to periclase Miller indices (111), (200), (220), (311) and (222) were observed, indi-

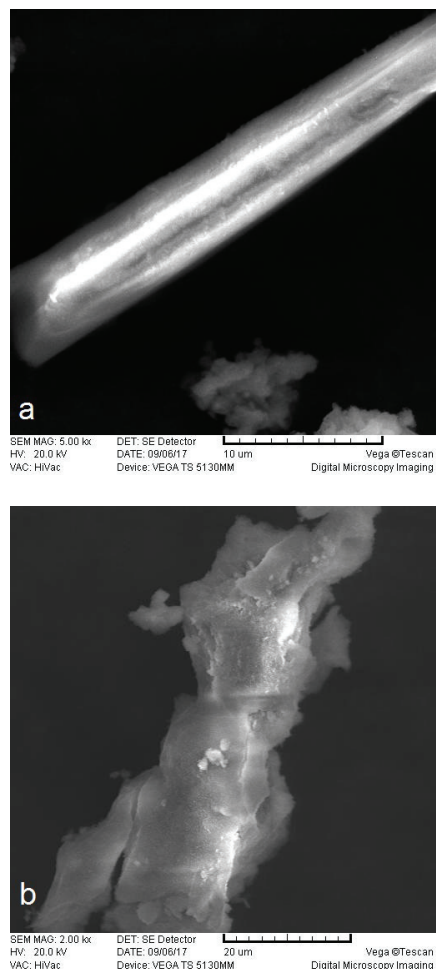


Figure 3. SEM micrographs of fibers obtained in coagulation bath at 70 °C: a) fiber:70/48, b) fiber:70/96h.

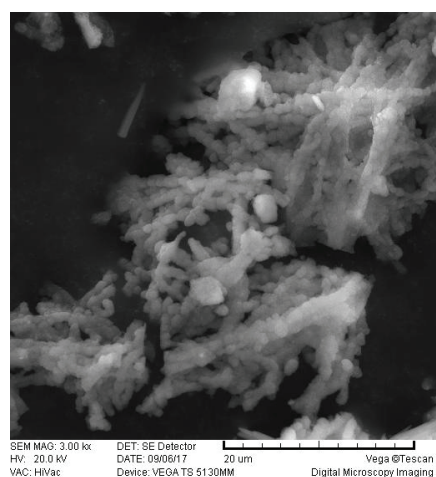


Figure 4. SEM micrograph of fiber: 90/48h.

ating that a single phase of MgO was formed after heat treatment. The upper patterns belong to the samples obtained after hydration treatment of MgO fibers. Synthesis of Mg(OH)<sub>2</sub> fibers along SS requires strictly manipulated conditions by means of tem-

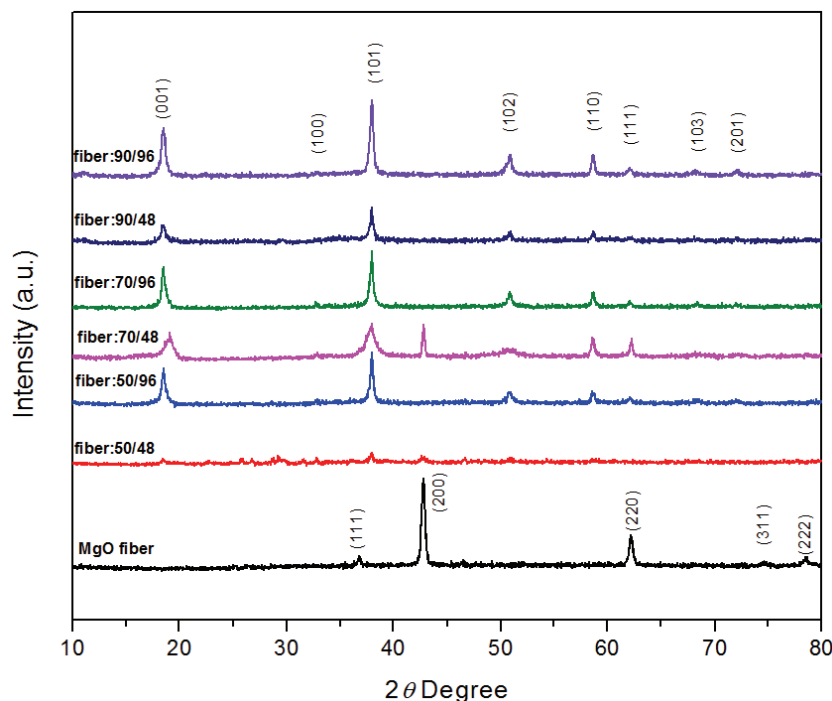


Figure 5. XRD patterns of periclase and brucite obtained by using spider silk as a template.

perature, incubation time and solvent control for obtaining the desired shape, size and the structure of crystals [31]. The labeled diffraction peaks correspond to brucite Miller indices (001), (100), (101), (102), (110), (111), (103) and (201), respectively (JCPDS 83-0114). However, samples: fiber:50/48h and fiber:70/48h were not single-phased. Lower intensity diffraction peaks belonging to periclase were present indicating that hydration process was not finished after the applied time of synthesis procedure. On the other hand, all the other samples consisted of pure brucite. Thus, for all samples, the incubation period of 96 h yielded pure brucite phase, while for the 48 h hydration, for the temperatures of 50 and 70 °C, the set time was not enough for complete crystallization of magnesium hydroxide. With increasing the temperature to 90 °C, crystallization was stimulated and incubation period was shortened to 48 h. Using the Scherrer's equation, the crystallite sizes of the samples were calculated from XRD patterns by extrapolating data from the most intensive indexed peaks – (200) for MgO fiber sample, and (101) for Mg(OH)<sub>2</sub> fiber samples:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum (FWHM),  $\theta$  is the Bragg angle for the studied peak/ring, and  $K$  is the shape factor. The results are presented in Table 1. It could be seen that the increase of incubation time contributed to the increase of crystallite size.

Table 1. Crystallite size of fibers obtained under different experimental conditions

Sample	Assignment	Miller Indices ( <i>hkl</i> )	Crystallite size nm
MgO fiber	Periclase	200	22.5
Fiber:50/48h	Brucite	101	20.3
Fiber:50/96h	Brucite	101	23.8
Fiber:70/48h	Brucite	101	7.2
Fiber:70/96h	Brucite	101	25.2
Fiber:90/48h	Brucite	101	21.5
Fiber:90/96h	Brucite	101	22.7

The novelty of this approach is that for the first time, natural fiber was used as a template for synthesis of magnesium oxide fibers. It would be also interesting to try obtaining MgO with different types of fibers, as well as the fibers with various diameters. The applied method is simple, low-cost, and uniform fibers were obtained without using organic additives or catalysts that are usually used in MgO and Mg(OH)<sub>2</sub> fabrication, hence the method is less hazardous, simpler, and more environmentally friendly compared to conventional. Also, for the first time Mg(OH)<sub>2</sub> fibers were obtained and obtaining conditions for brucite fibers were discussed. We believe that these results would contribute to development of novel generation of materials for insulation (MgO) and/or flame retardant (Mg(OH)<sub>2</sub>) applications.

## CONCLUSION

In this work, spider silk has been employed as a template for synthesis of fibrous MgO and Mg(OH)<sub>2</sub> by utilizing commonly used compound such as magnesium chloride (MgCl<sub>2</sub>). The synthesis process for obtaining MgO fibers was easy to operate, and this is a new approach for obtaining MgO fibers for insulation applications. The length and the diameter of fibers were determined by the dimensions of spider silk fibers that were chosen as a template. By hydration of MgO fibers in coagulation bath in different temperatures and incubation periods, brucite fiber-like structures were formed. Scanning electron microscopy showed that with increasing incubation time and/or temperature, the diameter of Mg-compounds-based fibers was increased. By heating dried spider silk previously immersed in the solution of MgCl<sub>2</sub>, single phase MgO was obtained, which was confirmed by the X-ray diffraction analysis. After hydrating as obtained MgO fibers, the Mg(OH)<sub>2</sub> crystals were formed on the surface of the fibers. XRD confirmed the presence of single-phased brucite for all the samples obtained after 96 h incubation, and for sample incubated at 90 °C for 48 h, indicating that longer incubation period and higher temperatures outcomes in pure brucite crystalline phase. For other samples obtained at lower temperatures and for shorter time (fiber:50/48h and fiber:70/48h), the crystallization process was not complete and periclase phase was also present. For the first time, fiber morphology is reported for brucite, and the uniformity of fibers allows possible utilization in refractory materials.

## Acknowledgment

This project was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project number: 45012).

## REFERENCES

- [1] Morales E, Lunsford JH. Oxidative dehydrogenation of ethane over a lithium-promoted magnesium oxide catalyst *J Catal* 1989; 118 (1): 255-265.
- [2] Nagaraja BM, Kumar VS, Shashikala V, Padmasri AH, Sreevardhan Reddy SS, Raju BD, Rama Rao KS. Effect of method of preparation of copper – magnesium oxide catalyst on the dehydrogenation of cyclohexanol. *J Mol Catal A: Chem*. 2004; 223: 339-345.
- [3] Guzman J, Gates BC. Structure and Reactivity of a Mononuclear Gold-Complex Catalyst Supported on Magnesium Oxide. *Angew Chem Int Ed*. 2003; 42(6): 690-693.
- [4] Oelerich W, Klassen T, Bormann R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J Alloys and Compd*. 2001; 315 (1–2): 237-242.
- [5] Kumar D, Reddy VB, Mishra BG, Rana RK, Nadagouda MN, Varma RS. Nanosized magnesium oxide as catalyst for the rapid and green synthesis of substituted 2-amino-2-chromenes. *Tetrahedron*. 2007; 63(15): 3093-3097.
- [6] Copp A. Magnesia/magnesite. *Am Ceram Soc bull*. 1995; 74(6): 135-137.
- [7] Yin D, Zhang Y, Zhang Y, Peng Z, Fan Y, Sun K. Reinforcement of peroxide-cured styrene–butadiene rubber vulcanizates by methacrylic acid and magnesium oxide. *J Appl Polym Sci*. 2002; 85(13): 2667-2676.
- [8] Bhargava A, Alarco JA, Mackinnon IDR, Page D, Ilyushchkin A. Synthesis and characterisation of nanoscale magnesium oxide powders and their application in thick films of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub>. *Mater Lett*. 1998; 34(3–6): 133-142.
- [9] Yuan YS, Wong MS, Wang SS. Solid-state processing and phase development of bulk (MgO)<sub>w</sub>/BPSCCO high-temperature superconducting composite. *J Mater Res*. 1996. 11(1): 8-17.
- [10] Chen D, Zhu L, Liu P, Zhang H, Xu K, Chen M. Rod-like morphological magnesium hydroxide and magnesium oxide via a wet coprecipitation process. *J Porous Mater*. 2009; 16(1): 13-18.
- [11] Kordas G. Sol-gel preparation of MgO fibers. *J Mater Chem*. 2000; 10(5): 1157-1160.
- [12] Chen YJ, Li JB, Han YS, Yang XY, Dai JH. Fabrication of decorated MgO crystalline fibers. *Mater Res Bull*. 2003; 38(3), 445-452.
- [13] Hota G, Ramakrishna S, Wun Jern N. One step fabrication of MgO solid and hollow submicrometar fibers via Electrospinning method. *Am Ceram Soc*. 2009; 92(10) 2429-2433.
- [14] Rocha SDF, Mansur MB, Ciminelli VST. Kinetics and mechanistic analysis of caustic magnesia hydration. *J Chem Technol Biotechnol*. 2004; 79(8): 816-821.
- [15] Holloway LR. Application of Magnesium Hydroxide as a Flame Retardant and Smoke Suppressant in Elastomers. *Rubber Chem Technol*. 1988; 61(2): 186-193.
- [16] Rocha SDF, Ciminelli VST. Utilization of Magnesium Hydroxide Produced by Magnesia Hydration as Fire Retardant for Nylon 6-6,6. *Polímeros*. 2001; 11: 116-120.
- [17] Lv J, Qiu L, Qu B. Controlled growth of three morphological structures of magnesium hydroxide nanoparticles by wet precipitation method. *J Cryst Growth*. 2004; 267(3-4): 676-684.
- [18] Lv J, Qiu L, Qu B. Controlled synthesis of magnesium hydroxide nanoparticles with different morphological structures and related properties in flame retardant ethylene-vinyl acetate blends. *Nanotechnology*. 2004; 15: 1576.
- [19] Yan C, Xue D, Zou L, Yan X, Wang W. Preparation of magnesium hydroxide nanoflowers. *J Cryst Growth*. 2005; 282(3-4): 448-454.
- [20] Annal GH, Kamath V. Electrochemical synthesis of metal oxides and hydroxides. *Chem Mater*. 2000; 12(5): 1195-1204.
- [21] Li Y, Sui M, Ding Y, Zhuang J, Wang C. Preparation of Mg(OH)<sub>2</sub> nanorods. *Adv Mater*. 2000; 12: 818-821.

- [22] Hao L, Zhu C, Mo X, Jiang W, Hu Y, Zhu Y, Chen Z. Preparation and characterization of Mg(OH)<sub>2</sub> nanorods by liquid-solid arc discharge technique. *Inorg Chem Commun.* 2003; 6(3): 229-232.
- [23] Zou G, Liu R, Chen W. Highly textural lamellar meso-structured magnesium hydroxide *via* a cathodic electro-deposition process. *Mater Lett.* 2007; 61(10): 1990-1993.
- [24] Doblhofer E, Heidebrecht A, Scheibel T. To spin or not to spin: spider silk fibers and more. *Appl Microbiol Biotechnol.* 2015; 99(22): 9361-9380.
- [25] Singh A, Hede S, Sastry M. Spider Silk as an Active Scaffold in the Assembly of Gold Nanoparticles and Application of the Gold–Silk Bioconjugate in Vapor Sensing. *Small.* 2007; 3(3): 466-473.
- [26] Mayes EL, Vollrath F, Mann S. Fabrication of Magnetic Spider Silk and Other Silk-Fiber Composites Using Inorganic Nanoparticles. *Adv Mater.* 1998; 10(10): 801-805.
- [27] Huang L, Wang H, Hayashi CY, Tian B, Zhao D, Yan Y. Single-strand spider silk templating for the formation of hierarchically ordered hollow mesoporous silica fibers. *J Mater Chem.* 2003; 13(4): 666-668.
- [28] Yan L, Zhuang J, Sun X, Deng Z, Li Y. Formation of rod-like Mg(OH)<sub>2</sub> nanocrystallites under hydrothermal conditions and the conversion to MgO nanorods by thermal dehydration. *Mater Chem Phys.* 2002; 76(2): 119-122.
- [29] Razouk R, Mikhail RS. The hydration of magnesium oxide from the vapor phase. *J Phys Chem.* 1958; 62(8): 920-925.
- [30] Henrist C, Mathieu JP, Vogels C, Rulmont A, Cloots R. Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. *J Cryst Growth.* 2003; 249(1–2): 321-330.
- [31] Fan W, Sun S, Song X, Zhang W, Yu H, Tan X, Cao G. Controlled synthesis of single-crystalline Mg(OH)<sub>2</sub> nanotubes and nanorods via a solvothermal process. *J Solid State Chem.* 2004; 177(7): 2329-2338.

## IZVOD

### SINTEZA VLAKANA MAGNEZIJUM-OKSIDA I MAGNEZIJUM-HIDROKSIDA KORIŠĆENJEM PAUKOVE MREŽE KAO MATRICE

Svetlana Dmitrović<sup>1</sup>, Marija Prekajski<sup>1</sup>, Bojan Jokić<sup>2</sup>, Goran Branković<sup>3</sup>, Aleksandra Zarubica<sup>4</sup>, Vladimir Žikić<sup>4</sup>, Branko Matović<sup>1</sup>

<sup>1</sup>Institut za nuklearne nauke „Vinča”, Univerzitet u Beogradu, p.pr. 522, 11000 Beograd, Srbija

<sup>2</sup>Tehnološko–metalurški fakultet, Univerzitet u Beogradu, Karnegijeva 4, 11000 Beograd, Srbija

<sup>3</sup>Institut za multidisciplinarna istraživanja, Odsek za nauku o materijalima, Univerzitet u Beogradu, Kneza Višeslava 1, 11000 Beograd, Srbija

<sup>4</sup>Prirodno–matematički fakultet, Univerzitet u Nišu, Višegradska 33, 18000 Niš, Srbija

(Naučni rad)

Vlakna paukove mreže sakupljena od *Pholcus phalangioides* pauka korišćena su kao matrica za dobijanje vlakana magnezijum oksida (MgO, periklas) i magnezijum-hidroksida (Mg(OH)<sub>2</sub>, brucit). Vlakna magnezijum oksida jednostavno su dobijena termičkim razlaganjem soli magnezijuma (MgCl<sub>2</sub>) u prisustvu vlakana paukove mreže, dok su vlakna magnezijum hidroksida sintetisana hidratacijom MgO vlakana na temperaturama: 50, 70 i 90 °C u trajanju od 48 i 96 h. Na osnovu rezultata skenirajuće elektronske mikroskopije (SEM), veličina sintetisanih MgO vlakana bila je određena dimenzijama vlakana pauka, dok je za Mg(OH)<sub>2</sub> vlakna prosečan dijametar rastao sa produženjem perioda hidratacije. Na površini Mg(OH)<sub>2</sub> vlakana uočeni su tabličasti kristali brucita. Difrakcija X zraka (XRD) pokazala je da su vlakna periklasa jednofazna (dobijen je čist magnezijum-oksidi), dok su brucitna vlakna bila dvofazna ili jednofazna, u zavisnosti od inkubacionog perioda i/ili temperature na kojoj je vršena inkubacija.

**Ključne reči:** Brucit • Periklas • Vlakna • Vlakna paukove mreže