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

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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 ($Mg(OH)_2$, brucite) fibers. Magnesium oxide fibers were obtained in a simple manner by heat induced decomposition of magnesium salt ($MgCl_2$) 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 $Mg(OH)_2$ fibers, the average diameter was increased with prolonging the hydration period. The surface of $Mg(OH)_2$ 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 $Mg(OH)_2$ fibers were two- or single-phased brucite depending on incubation period, and/or incubation temperature.

Keywords: brucite, periclase, fibers, spider silk.

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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, electrospining [11–13], yet no obtaining MgO fibers by natural fiber as a template has been reported in literature.

Magnesium hydroxide ($Mg(OH)_2$, 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 morphology, 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 $Mg(OH)_2$ by various techniques like hydrothermal, sol–gel, wet precipitation or electrochemical synthesis [17–23]. By reviewing the literature, no data for obtaining $Mg(OH)_2$ 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 ($MgCl_2$) 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.

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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 ($MgCl_2 \cdot H_2O$, 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 $Mg(OH)_2$ 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 CuKα1 radiation (λ = 0.1540 nm, operating at 40 kV and 40 mA). XRD data were collected from 10 to 80° (2θ) 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 $Mg(OH)_2$ 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 $MgCl_2$ 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:

$$MgCl_2 + ½O_2 \rightarrow MgO + Cl_2\uparrow$$

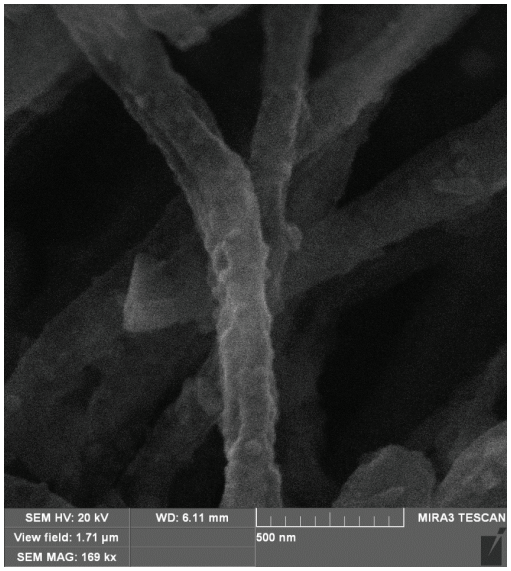

Figure 1. FESEM image of MgO fibers obtained via using spider silk as a template.

Hydrating magnesia is a common process for obtaining $Mg(OH)_2$, and hydration conditions are of special importance for designing $Mg(OH)_2$ 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:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

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].

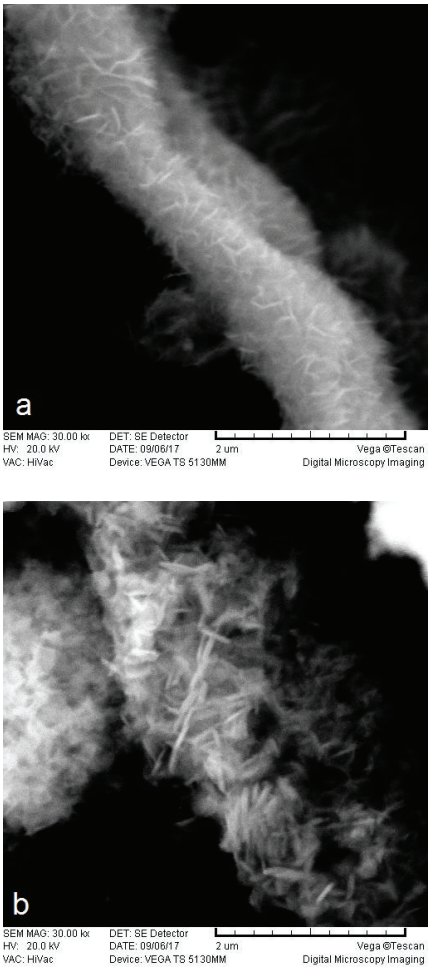

Figure 2. SEM micrographs of fibers obtained in coagulation bath at 50 °C: a) fiber: 50/48 and b) fiber:50/96h.

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 $Mg(OH)_2$ 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, indicating 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 $Mg(OH)_2$ fibers along SS requires strictly manipulated conditions by means of tem-

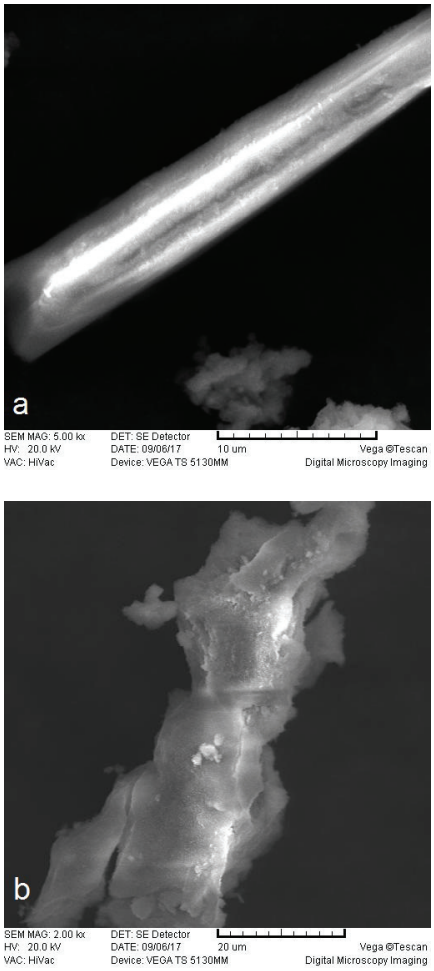

Figure 3. SEM micrographs of fibers obtained in coagulation bath at 70 °C: a) fiber:70/48, b) fiber:70/96h.

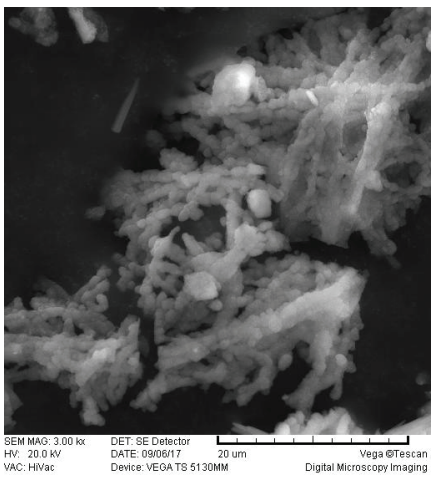

Figure 4. SEM micrograph of fiber: 90/48h.

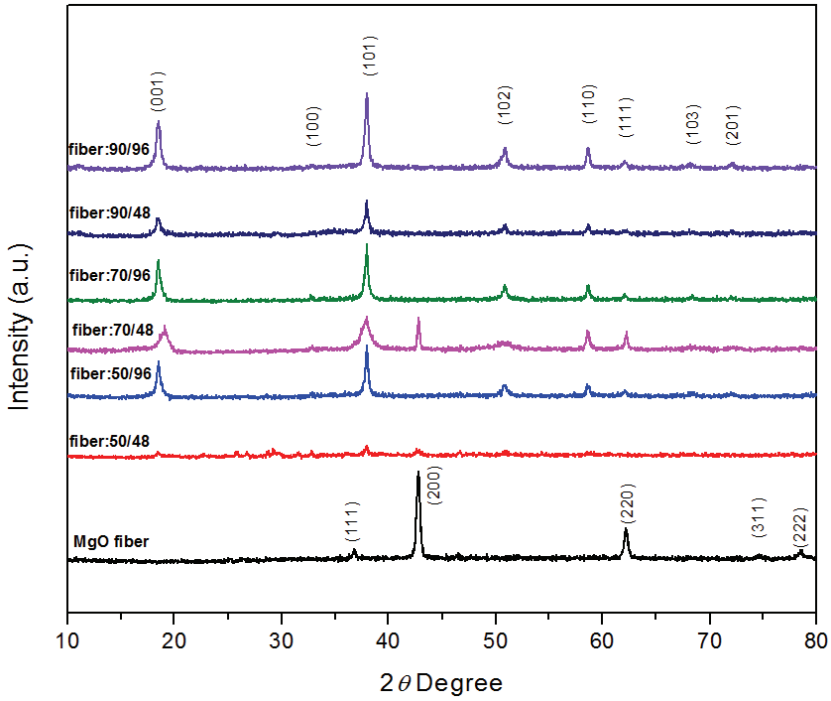

Figure 5. XRD patterns of periclase and brucite obtained by using spider silk as a template.

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 hydratation, 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 $Mg(OH)_2$ fiber samples:

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

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM), θ 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 (*hkl*)	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 $Mg(OH)_2$ fabrication, hence the method is less hazardous, simpler, and more environmentally friendly compared to conventional. Also, for the first time $Mg(OH)_2$ 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 ($Mg(OH)_2$) applications.

CONCLUSION

In this work, spider silk has been employed as a template for synthesis of fibrous MgO and $Mg(OH)_2$ by utilizing commonly used compound such as magnesium chloride ($MgCl_2$). 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 $MgCl_2$, single phase MgO was obtained, which was confirmed by the X-ray diffraction analysis. After hydrating as obtained MgO fibers, the $Mg(OH)_2$ 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.

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IZVOD

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

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(Naučni rad)

Vlakna paukove mreže sakupljena od *Pholcus phalangioides* pauka korišćena su kao matrica za dobijanje vlakana magnezijum oksida (MgO, periklas) i magnezijum-hidroksida ($Mg(OH)_2$, brucit). Vlakna magnezijum oksida jednostavno su dobijena termičkim razlaganjem soli magnezijuma ($MgCl_2$) 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 $Mg(OH)_2$ vlakna prosečan dijametar rastao sa produženjem perioda hidratacije. Na površini $Mg(OH)_2$ vlakana uočeni su tabličasti kristali brucita. Difrakcija X zraka (XRD) pokazala je da su vlakna periklasa jednofazna (dobijen je čist magnezijum-oksid), dok su brucitna vlakna bila dvofazna ili jednofazna, u zavisnosti od inkubacionog perioda i/ili teperature na kojoj je vršena inkubacija.

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