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Tailoring of MgO/Mg(OH)$_2$ structures by molten salt electrolysis

Formiranje MgO/Mg(OH)$_2$ struktura elektrolizom iz rastopa

Nataša M. Vukićević*

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Abstract

The magnesium oxide (MgO)/magnesium hydroxide (Mg(OH)$_2$) nanostructures aside from showing high surface area, good thermal, electrical, optical and chemical characteristics, are also low-cost materials of benign nature with minimal environmental impact, which make them suitable for various application. Due to their specific properties magnesium oxide and magnesium hydroxide are used in medicine, sensors, solar cells, drinking and waste water treatments. Depending on the in advance planned application, considerable attention should be paid to the formation of appropriate magnesium oxide/hydroxide composition and surface morphology. Herein, a novel approach was used to the synthesis of MgO/Mg(OH)$_2$ structures by electrochemical deposition from magnesium nitrate hexahydrate melt onto glassy carbon. Galvanostatic and potentiostaic regimes of electrolysis were employed for direct formation of magnesium oxide. Morphology of the composed structures were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Analysis of the deposits made by both electrolysis regimes recognized formation of magnesium oxide as well as magnesium hydroxide. Comparative study of the deposits morphology showed that nano-sized needles and holes are produced by applied electrodepositions. Most of the needles formed participate in flower-like shapes. The holes observed in the deposit are a product of the hydrogen evolution and in the number, shape and size strongly depend on the deposition parameters applied. During controlled working potential or current density, the detached hydrogen bubbles produced different types of deposit structures, from dish-like to those of the honeycomb-like shape. Formation mechanism of the observed deposits is discussed.

Keywords: *magnesium oxide/hydroxide; nitrate melt; honeycomb-like structures; SEM; deposition*

Izvod

Nanostrukture magnezijum oksida (MgO)/magnezijum hidroksida (Mg(OH)$_2$) usled velike specifične površine, dobri termalnih, optičkih, električnih i hemijskih karakteristika predstavljaju jeftin materijal sa minimalnim uticajem na životnu sredinu, što im obezbeđuje veoma raznovrsnu primenu. Zahvaljući karakterističnim svojstvima magnezijum oksid i magnezijum hidroksid imaju značajnu primenu u medicini, senzorima, solarnim ćelijama, remedijaciji i prečišavanju pijaćih i otpadnih voda. U zavisnosti od planirane primene izuzetan značaj se pridaje formiranju oksida i hidroksida magnezijuma odgovarajućih sastava i površinske morfologije. U ovom radu predstavljen je novi pristup u sintezi MgO/Mg(OH)$_2$ nanostruktura elektrohemijskim taloženjem iz rastopa magnezijum nitrata heksahidrata na staklastom ugljeniku. Za direktno nastajanje magnezijum oksida korišćeno je galvanostatsko i potenciostatsko taloženje. Morfologije dobijenih struktura taloga analizirane su skenirajućom elektronskom mikroskopijom (SEM), energetskom disperzivnom spektroskopijom (EDS) i difrakcijom X-zraka (XRD). Nezavisno od primenjene tehnike elektrohemijskog taloženja formirani talozi sastoje se kako od magnezijum oksida tako i od magnezijum hidroksida. Uporednom analizom morfoloških struktura taloga nastalih primenom obe tehnihe elektrohemijskog taloženja pokazano je da se kreirane morfološke forme uglavnom sastoje od nano iglica i rupa (praznina u formiranom talogu). Igličaste nanostrukture se pretežno grupišu u aglomerate cvetnog oblika. Rupe nastaju kao produkt razvijanja vodonika, a njihov broj, veličina i oblik je u direktnoj zavisnosti od

parametara elektrohemijskog taloženja. Tokom kontrolisanog taloženja (kontrolisan potencijal ili gustina struje taloženja) izdvajanje vodonika može uticati na formiranje različitih morfoloških formi igličastog taloga, od oblika posuda do kompleksnijih struktura oblika saća. Mehanizam nastajanja navedenih oblika taloga je predložen i diskutovan u ovom radu.
Ključne reči: *magnezijum oksid/hidroksid; rastop nitrata; structure nalik saću; SEM; taloženje*

Introduction

Intensive efforts over the past decade have been devoted to research of nanomaterials with unique features and controllable morphology. Moreover, it is worth noting that morphologically adjusted properties play an essential role since, behavior and activity of nanoparticles largely depends on their shape and size. The magnesium oxide (MgO)/magnesium hydroxide ($Mg(OH)_2$) are low-cost, non-poisonous, thermally stable materials with minimal environmental impact [1,2]. Thus, magnesium oxide and magnesium hydroxide have many industrial applications in the field of sensors, solar cells, green and medical technology [1,2]. Considerable attention is paid to the formation of nanostructured $MgO/Mg(OH)_2$ with different nano-dimension and various shapes, because it is noticed that morphologically tailor made properties play an important role in future application. Several methods have been exploited to produce magnesium oxide and/or magnesium hydroxide nanoparticles with characteristic surface morphology: pulsed laser deposition [3], precipitation [4] electrodeposition from aqueous solution [5], sol-gel [6] and ultrasonic methods [6]. However, to obtain MgO or/and $Mg(OH)_2$ is rather difficult without adding different additives, precursors and further annealing [4-7]. Generally, it is a fact that electrochemical deposition offers an easy controlled and useful method for obtaining nano-sized deposits. Therefore, electrodeposition offers good possibilities for properties control of the deposited material. Our latest investigation on the electrochemical deposition of $MgO/Mg(OH)_2$ nanostructures from magnesium nitrate hexahydrate melt showed that MgO and $Mg(OH)_2$ can be directly synthesized from the used melt onto glassy carbon working electrode [8-10]. Depending on the type of electrolysis, galvanostatic or potentiostatic regime, different shape and size of deposit can be obtained. It was found that during both methods of the electrodeposition needle-like, flower-like deposit forms and honeycomb-like structures can be produced. We continued our studies focusing on the adjusting necessary parameters for productions of specified forms. This work presents comparative study of the morphological forms produced during both technics of the electrodeposition. Focus is given on conditions for the electrochemical deposition of in advance tailored morphological forms as well as on formation mechanism of the observed deposits.

Experimental

Electrochemical experiments were performed in a three-electrode Pyrex glass cell under argon atmosphere at 100 °C. Glassy carbon (GC, Alfa Aeser-Johnson Mathey Co, USA) with an active surface area of 1 cm^2 served as a working electrode. Mg wire (3 mm in diameter) and Mg plate (surface area 7.5 cm^2) (99.999%, Luoyang Magnesium Gurnee Metal Material Company. Ltd, Henan, China) were used as the reference and counter electrode, respectively. All reported potentials were referred to the Mg/Mg^{2+}. Before any experiment electrodes were freshly prepared in the way described in detailed elsewhere [8-10]. The electrolyte was made from magnesium nitrate hexahydrate ($Mg(NO_3)_2\cdot 6H_2O$, J.T. Baker, The Netherlands), used as received. The electrochemical experiments were realized by Potentiostat/Galvanostat Model 273A, (Princeton Applied Research, Oak Ridge, TN, USA) regulated by accompanying software (Power Suite software).
In order to investigate influences of electrochemical deposition parameters on the formation of magnesium oxide/hydroxide morphological forms galvanostatic and potentiostaic regimes of electrolysis were employed.
The galvanostatic electrodeposition was realized using:

– the same amount of total charge passed during the deposition (Q = 4 C) under different current density of i = 2, 4 or 6 mA cm^{-2}, and
– the same current density, i = 4 mA cm^{-2}, but different amounts of deposition charge used (Q = 1, 2 and 4 C).
The potentiostatic electrodeposition was realized under regime in:
-magnesium UPD region: 700 mV, 5 mV *vs.* Mg/Mg^{2+}
-magnesium OPD region: -200 mV, -700mV, -1000 mV *vs.* Mg/Mg^{2+}.
The chosen deposition potential was applied for 30 or 120min.
After deposition the working electrode was rinsed with absolute ethanol (Zorka-Pharma, Šabac, Serbia) and dried at room temperature. Morphology of the obtained structures were characterized by scanning electron microscopy (SEM, TESCAN Digital Microscope; model VEGA3, Brno, Czech Republic) coupled with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was used for the analysis of the tailored deposits using Philips PW 1050 powder diffractometer at room temperature with Ni filtered CuK_α radiation (λ = 1.54178 Å), scintillation detector within 15–75° 2θ range in steps of 0.05°, and scanning time of 5 s per step.

Results and Discussion

Fig. 1 displays common morphological forms of the deposits obtained onto glassy carbon working electrode from magnesium nitrate hexahydrate melt at an underpotential of 700 mV *vs.* Mg/Mg^{2+} and at overpotential of – 200 mV *vs.* Mg/Mg^{2+} after 30 min of deposition. Typical magnesium oxide/hydroxide nano-sized structures produced in Mg OPD region after 2 h of deposition are presented in Fig. 2. A structure of the intertwined thin needles, frequently called whiskers [11], formed under the booth potentials applied, are seen in Fig.1. However, contrary to the working electrode surface exposed to the potential in the UP region (Fig. 1a), under higher cathodic overpotentials, (Figs. 1b-c and Fig. 2), the whole surface of the working electrode is covered with deposit, and apart from the needles there are holes formed in the deposit made by hydrogen evolution reaction. Very thin needles form flower-like agglomerates see Fig. 1b and 2b. Also, very porous honeycomb-like structure [12] with individual holes and flower-like structures are formed, Fig. 1c, 2b-c.

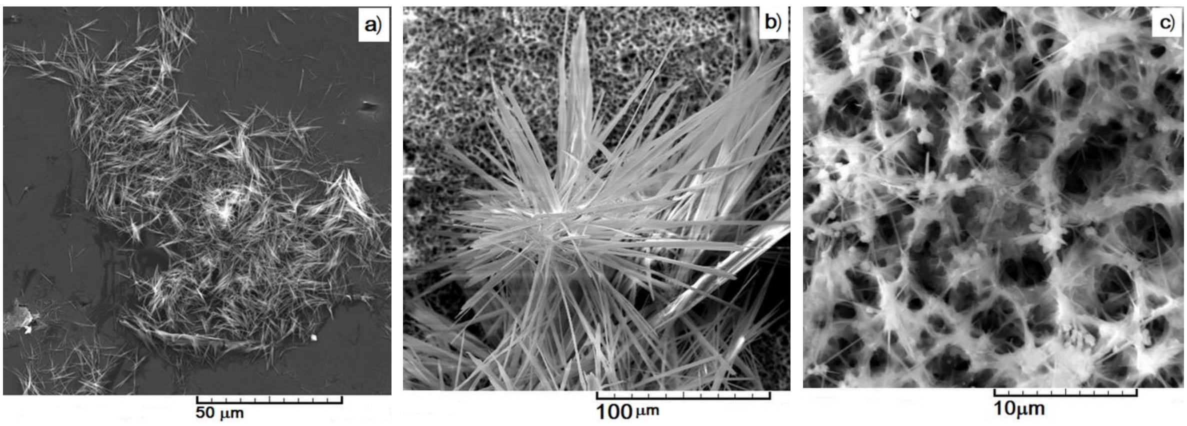

Figure 1. *SEM images on GC electrode from magnesium nitrate hexahydrate melt at 100°C at constant potentials for 30 min at: a) 700 mV; b)and c) – 200 mV vs.* Mg/Mg^{2+}.

With prolonged time of electrodeposition, Fig. 2a and at even higher overpotential Fig. 2b-c dominant morphological forms produced are holes formed from detached hydrogen bubbles and the thin needles. It can be noticed that with longer electrodeposition time denser network from thin needles around the holes are obtained. The deposit obtained at – 0.200 V *vs.* Mg/Mg^{2+} was analysed by EDS and the chemical composition of structure is shown in the Fig. 3.

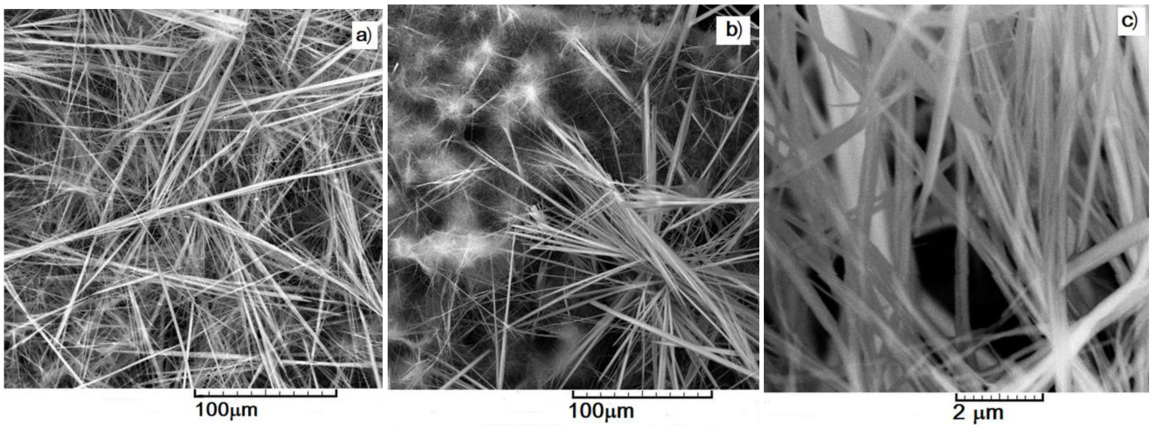

Figure 2. *SEM images on GC electrode from magnesium nitrate hexahydrate melt at 100°C at constant potentials for 120 min at: a) – 200 mV; b) and c) – 1000 mV vs. Mg/Mg^{2+}.*

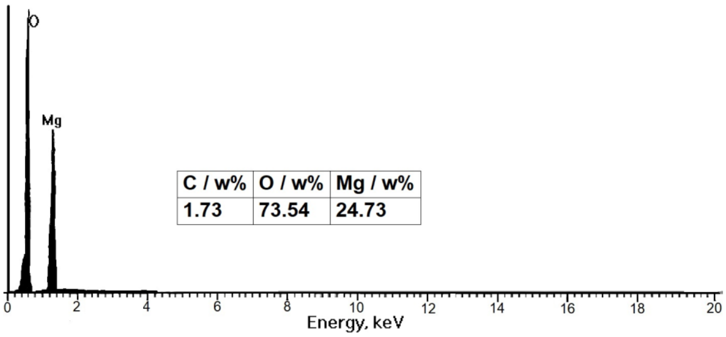

Figure 3. *EDS analysis performed from samples given in Fig. 2b.*

The electrochemical and chemical reactions, as well as probable electrochemical mechanism for the formation of $MgO/Mg(OH)_2$ on the working electrode as a result of electrodeposition process is described and discussed in our earlier work [8,10,13]. Various morphologies are the result of numerous reactions including hydrogen evolution at more negative potentials [8,10,13]. We continued our studies focusing on monitoring different parameters during galvanostatic electrolysis, deposition charge or current density. Morphological forms of MgO and $Mg(OH)_2$ produced with applied current densities of 2, 4 and 6 mA cm^{-2} with restricted amount of total charge passed during the deposition to 4 C are given in Fig. 4.

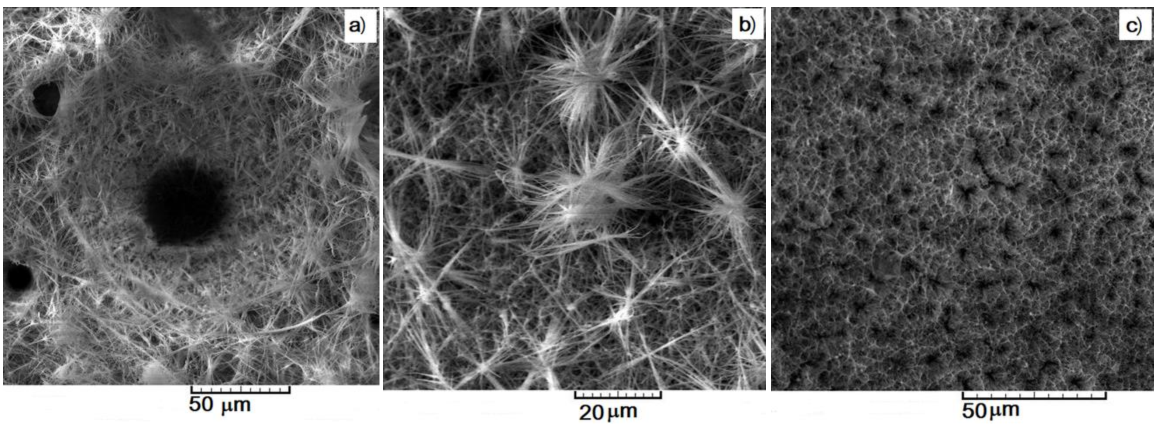

Figure 4. *SEM images on GC electrode from magnesium nitrate hexahydrate melt at 100°C obtained with an amount of passed electricity of 4 C at current density of: a) 2 mA cm^{-2}; b) 4 mA cm^{-2}; c) 6 mA cm^{-2}.*

It can been notised that during deposition with electricity restricted to 4 C the main morphologycal forms obtained with the current density of 2 mA cm^{-2} and 4 mA cm^{-2} were holes, formed from the detached hydrogen bubbles, and the flower-like forms created from thin needles, Fig. 4a-b and Fig. 5c. Further rise of applied current density to 6 mA cm^{-2} shows an obvious impact on the enhanced hydrogen evolution reaction, which leads to enlarged number of holes but also to the reduction in their diameter, favouring formation of the honeycomb-like structures, Fig. 4c. The influence of the amount of charge passed at the time of deposition on the tailored structures is examined at a current density of 4 mA cm^{-2}, Fig. 5. From Fig. 5 it is visible that flower-like forms made from very long needles oriented in all directions are dominant under the chosen conditions.

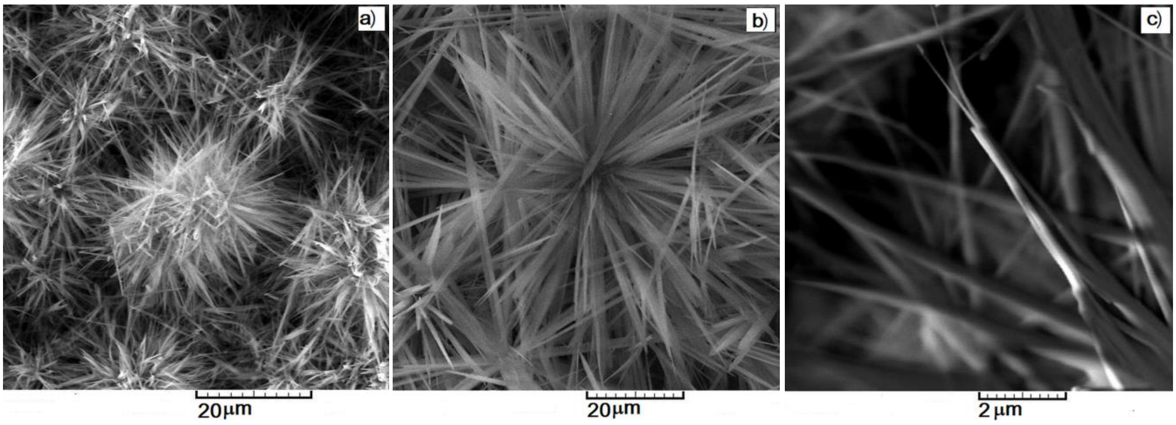

Figure 5. *SEM images on GC electrode from magnesium nitrate hexahydrate melt at 100°C obtained with constant current density of 4 mA cm^{-2} with charge of: a) 1 C; b)2 C; c) 4 C.*

Conclusion

An electrochemical route for production of well-controlled MgO and $Mg(OH)_2$ deposited structures from magnesium nitrate hexahydrate melt onto glassy carbon at 100°C is presented. Galvanostatic and potentiostaic regimes of electrodeposition were used for possible direct synthesis of magnesium oxide. Morphological forms of tailored $MgO/Mg(OH)_2$ structures produced by the galvanostatic regime of electrolysis are seemingly complementary to those obtained by the potentiostatic electrodeposition. In both cases, nano-sized needles oriented in all directions produce flower-like shapes and holes generated from detached hydrogen bubbles of several shapes and sizes were obtained. It was established that the honeycomb-like structures were constructed from the holes enclosed with very thin intertwined needles. The shape, number and size strongly depend on the deposition parameters applied. It was shown that when controlling a chosen parameter of the deposition it is possible to force the formation of in advance tailored $MgO/Mg(OH)_2$ structures, which should be beneficial for their application since it largely depends on its morphological forms.

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