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Synthesis and characterization of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite and their application for preparation of zinc phosphate dental cement

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ABSTRACT

We report here the synthesis of nanoparticles of ZnO and MgO and ZnO/MgO nanocomposite through reactions of zinc acetate and magnesium acetate solutions with tetramethylammonium hydroxide (TMAH) solution in the presence of polyvinyl pyrrolidone (PVP) by sonochemical method. At first, nanoparticles of ZnO and MgO were synthesized by the reaction of $Zn(CHCOO_3)_2$ and $Mg(CHCOO_3)_2$ with TMAH in the presence of PVP and constant frequency ultrasonic waves. Then, ZnO/MgO nanocomposite was prepared through reaction of magnesium acetate with TMAH in the presence of ZnO nanoparticles and PVP as structure director using ultrasonic-assisted method. The effects of different parameters on particle size and morphology of final ZnO and MgO powders and ZnO/MgO nanocomposite were optimized by 'one at a time' method. Both synthesized ZnO and MgO nanoparticles and ZnO/MgO nanocomposite were successfully applied to the preparation of zinc phosphate dental cement.

KEYWORDS

Sonochemical method;
Nanoparticles;
ZnO/MgO Nanocomposite;
Zinc phosphate dental cement.

INTRODUCTION

The synthesis and characterization of nanostructured oxide materials is in the focus of many recent and current research projects. This is due to the unique properties exhibited by nanoparticles in comparison to bulk material[1,2]. The metal oxides are extremely important technological materials for use in electronic and photonic devices and as catalyst in chemical industries. In recent years, researchers have focused more on the synthesis of both nanoparticles and nanocomposite of ZnO and MgO due to their application in advanced technologies. Many different physical and chemical techniques, such as chemical vapor deposition[3], thermal decomposition[4], sol–gel[5,6], co-catalyzed process[7], precipitation[8], spray pyrolysis[9], plasma torch[10], pulsed laser deposition[11] and hydrothermal synthesis[12] have been employed to prepare nano-sized ZnO and

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MgO particles. Several techniques have been also developed to prepare nanocomposite of ZnO/MgO. This nanocomposite has attracted much attention because it has a larger band gap than ZnO[13-16]. However, most of the techniques need highly temperatures and perform under a costly inert atmosphere. Our goal in this research is to suggest an easy method to synthesize more porous and spongy nanostructured zinc oxide and magnesium oxide and their nanocomposite. Such structures can be useful in active materials of dental cements.

One of the oldest and most widely used cements is zinc phosphate cement. This cement is a good choice for routine prosthodontic use; has a long, positive clinical history. Zinc phosphate cements are the strongest among the dental cements. They are principally used as luting cement for the cementation of inlays and other restorations fabricated outside of the mouth due to easy handling characteristics and adequate retentive properties[17]. The present study was intended to use a new and easy method for preparation of homogeneous porous nano-sized ZnO and MgO particles. For this purpose, fixed frequency ultrasonic waves were applied to prevented growth and helped formation of nanoparticles. In addition, polyvinyl pyrrolidone (PVP) was used as a structure director additive. This is the first report on sonochemical synthesis method of ZnO and MgO nano-powders and ZnO/MgO nanocomposite and their application to the preparation of zinc phosphate dental cement. The mechanical strength property of this cement is more than two commercially available phosphate cements.

EXPERIMENTAL

All the chemicals were obtained from Merck and they were used without further purification.

First, 50mL zinc acetate solution (0.10M) including PVP (10g/L) as structure director additive was sonicated for 30 min and then, enough volume of TMAH solution (0.28 M) was slowly added (similar to titration method). In this step, nano-structured zinc hydroxide was formed during the following reaction (1):

$$Zn(CH_3COO)_{2(aq)} + 2(CH_3)_4N(OH)_{(aq)} \downarrow Zn(OH)_{2(s)} + 2(CH_3COO)N(CH_3)_{4(aq)} \quad (1)$$

At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. The precipitated zinc hydroxide was filtered and washed with distilled water and ethanol for three times. To the obtained precipitate was added 50mL ethanol and the mixture was sonicated by ultrasonic instrument (Elma S60H model, 40 kHz) for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 320°C in a furnace for 2 h.

The following reaction (2) took place in the dehydration phase:

$$Zn(OH)_{2(s)} \rightarrow ZnO_{(s)} + H_2O_{(g)} \quad (2)$$

At dehydration phase, nanostructured zinc oxide was formed. The nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110°C. The final product was obtained in powder form. The nanostructured zinc oxide powder was characterized with a Brake-AXS D8 X-ray Advance Diffractometer using Cu K_α radiation source and a graphite monochromator (k = 1.54178 A°) and FT-IR spectroscopy (SHIMADZU–IR PRESTIGE 21 spectrometer) in a KBr matrix.. The morphology and size of the products were observed by Philips XL30 model scanning electron microscopy (SEM).

For Synthesis of nano-structured MgO, 50mL magnesium acetate solution (0.14 M) including PVP (10g/L) as structure director additive was sonicated for 30 min and then, enough volume of TMAH solution (0.34 M) was slowly added (similar to titration method). In this step, nano-structured magnesium hydroxide was formed during the following reaction (3):

$$Mg(CH_3COO)_{2(aq)} + 2(CH_3)_4N(OH)_{(aq)} \downarrow Mg(OH)_{2(s)} + 2(CH_3COO)N(CH_3)_{4(aq)} \quad (3)$$

At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. The precipitated magnesium hydroxide was filtered and washed with distilled water and ethanol for three times. To the resulted precipitate was added 50 mL ethanol and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 550°C in a furnace for 4 h.

The following reaction (4) took place during the dehydration phase:

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)} \quad (4)$$

The MgO nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110°C. The final product was obtained in nanopowder form. The nanostructured magnesium oxide powder was characterized by SEM, XRD and FT-IR spectroscopy.

For Synthesis of ZnO/MgO nanocomposite, a 50-mL aliquot containing magnesium acetate solution (0.17 M) and 3.44g of ZnO nanopowder and PVP (10g/L) was sonicated for 30 min and then, 7.5mL of TMAH solution (0.28 M) was slowly added. In this step, nanostructured magnesium hydroxide was formed.

$$ZnO_{\text{nanopowder}} + Mg(OH)_{2\,(s)\,\text{nanosized}} \downarrow$$

$$ZnO/MgO_{\text{nanocomposite}} + H_2O_{(g)} \quad (5)$$

At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. To form the ZnO/MgO nanocomposite (5), the obtained precipitate was dehydrated at 550°C in a furnace for 4 h.

The ZnO/MgO nanocomposite was sonicated in ethanol for 30 min to eliminate agglomeration. For vaporization of solvent, nanopowder was heated to 110°C. The ZnO/MgO nanocomposite powder was characterized by SEM, XRD and FT-IR spectroscopy.

For dental cement preparation, required amounts of ZnO and MgO nanoparticles and/or ZnO/MgO nanocomposite, silica fused and aluminum oxide were mixed together in a crucible based on the formulation of the zinc phosphate dental cements preparation (TABLE 1). The mixture was heated to 1050°C in the furnace for 5 h. Then various amounts of liquid of Harvard zinc phosphate dental cement was slowly added to this mixture. After adding liquid, the mixture was additionally mixed for 1-2 min. The prepared paste was poured into cylindrical mold (6mm diameter and 12mm deep). The mechanical strength of the cement specimens was measured using a universal testing machine (Zwick Z250 model) with a crosshead speed of 1 mm/min.

RESULTS AND DISCUSSION

The aim of this work is to synthesize ZnO and MgO nanoparticles and ZnO/MgO nanocomposite in order to obtain the higher mechanical strength than commercial dental cement of zinc phosphate. The parameters including ultrasonic wave, concentrations of $Zn(CHCOO_3)_2$, $Mg(CHCOO_3)_2$, TMAH and PVP, and synthesis temperature were optimized using "one at a time" method[18].

Two synthesis processes were carried out (i) in the presence and (ii) absence of ultrasonic waves at the same temperature and concentrations of $Zn(CHCOO_3)_2$, $Mg(CHCOO_3)_2$ and TMAH in the absence of structure director additives. SEM images of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite show that the ultrasonic waves make both ZnO and MgO nanoparticles and their nanocomposite more uniform and small (Figure 1)

Six synthetic processes were followed at 20, 30, 50, 60, 70 and 80°C so that the effect of synthesis temperature on morphology and particle size of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite can be investigated. The SEM images showed that at temperatures of 30, 60 and 60C, smaller and more uniform ZnO and MgO nanoparticles samples and ZnO/MgO nanocomposite samples respectively were synthesized, probably because of the fact that at these temperatures, growth rate, nucleation rate and agglomeration rate are suitable for formation of optimum powders. Therefore, the temperatures of 30, 60 and 60°C were selected as the optimum temperatures for synthesis of ZnO, MgO nanoparticles and ZnO/MgO nanocomposite, respectively.

After confirming positive effect of ultrasonication, at 30°C and 0.20 M TMAH, the concentration of zinc and magnesium acetate solutions was varied from 0.06 to 0.28 M. Morphology and particle size of each compound was studied by SEM. The SEM results showed

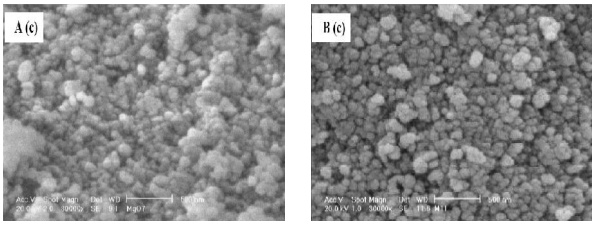

Figure 1 : SEM images of (a) ZnO and (b) MgO nanoparticles and ZnO/MgO nanocomposite (c) synthesized in the absence (A) and in the presence (B) of ultrasonic waves. Other conditions were constant as follows: synthesis temperature 30°C, 0.06 M zinc acetate, 0.10 M magnesium acetate, 0.20 M TMAH and 0.0 M PVP

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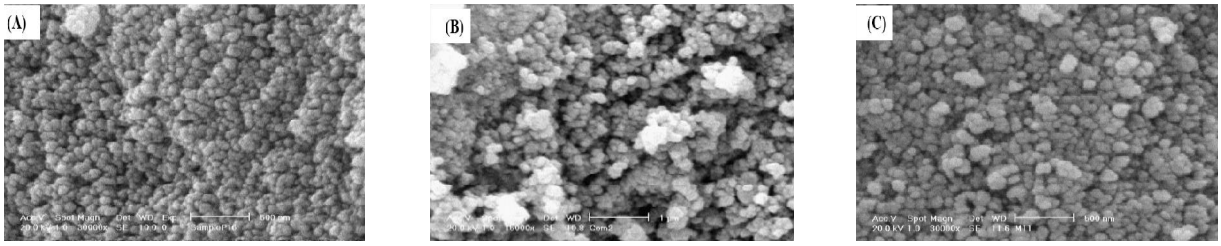
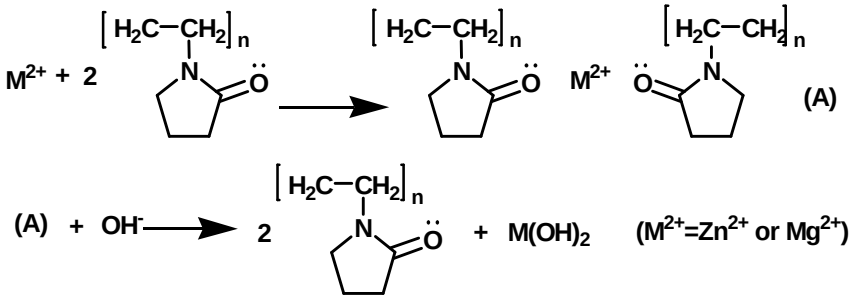


Figure 2 : SEM images of three samples (A) ZnO, and (B) MgO nanoparticles and (C) ZnO/MgO nanocomposite synthesized in optimum conditions and in the presence of ultrasonic waves: concentration of zinc acetate is 0.10 M, magnesium acetate is 0.14 M, TMAH is 0.28 and ZnO and MgO are 0.34 M, PVP is 10 g/L. Temperatures are 30, 60 and 60°C for ZnO and MgO nanoparticles and ZnO/MgO nanocomposite, respectively



Scheme : Structure of suggested complex for interaction between PVP and metallic ions (Zn^{2+} or Mg^{2+})

that concentrations of 0.10 and 0.14 M zinc acetate and magnesium acetate, respectively, produces more uniform and smaller particles. It can be concluded that at low concentrations of zinc (<0.10 M) and magnesium (<0.14 M) ions, the rate of particle growth is less than the rate of nucleation while at higher concentrations of zinc (>0.10 M) and magnesium (>0.14 M) ions, growth and agglomeration and other mechanisms involved in the formation of heavy particles are more manifest. Therefore, the concentrations of 0.10 and 0.14 M solutions of zinc acetate and magnesium acetate, respectively, were selected as the optimum concentrations.

Different alkaline solutions such as NaOH, Na_2CO_3, NH_4OH and TMAH solutions at various concentrations were investigated to produce smaller and uniform particles of ZnO, MgO and ZnO/MgO nanocomposite. The SEM images of synthesized samples showed that TMAH is a suitable alkaline for our purpose. The effect of TMAH concentration on particle size and morphology was investigated by SEM. The TMAH concentration was varied from 0.17 to 0.50 M. The SEM images of synthesized samples revealed that smaller and uniform nanoparticles of ZnO, MgO and nanocomposite of ZnO/MgO, can be formed at TMAH concentrations of 0.28, 0.34, and 0.34 M respectively. Lower concentrations of TMAH make high growth rate for precipitation particles and, at higher concentrations, there are some processes such as coagulation and agglomeration that makes bigger precipitation particles. Therefore, the TMAH concentrations of 0.28, 0.34 and 0.34 M were selected as the optimum concentration for synthesis of ZnO, MgO nanoparticles and ZnO/MgO nanocomposite, respectively.

There are some reports on the positive effects of PVP as structure director additive on the formation of suitable products[19-21]. According to these reports, PVP played an important role in determining the morphology of the products. Zhang et al.[22] reported that PVP probably organizes the nanostructures by forming a cation–PVP complex (Scheme). The suggested complex can prevent particles from growing. The probable mechanisms based on the suggested complex can be expressed as Scheme. The SEM images of synthesized samples showed that PVP, as a structure director, organizes uniformly the nanostructure of both zinc oxide and magnesium oxide in smaller sizes. Finally, 5 different concentrations of PVP (from 5 to 25g/L) in synthesis solution were examined in order to obtaining the best structure for the final products (ZnO and MgO nanoparticles and ZnO/MgO nanocomposite). As it shown in figure 2, at PVP concentration of about 10 g/L, both nanoparticles and nanocomposite can be synthesized in excellent and more porous nanostructure

TABLE 1 : Formulation of the powder for the zinc phosphate dental cement

No.	Compound†	Wt (%)	Compound‡	Wt (%)
1	Zinc oxide	86.0	ZnO/MgO nanocomposite	92.8
2	Magnesium oxide	8.6	Silica fused	4.3
3	Silica fused	3.0	Aluminum oxide	2.9
4	Aluminum oxide	2.4	-	-

Compound percents of ZnO and MgO powders are similar for both commercial powder and synthesized nanopowder. Compound percent of ZnO/MgO nanocomposite is the best percent that the mechanical strength amount was more than other ratios

(moss shape). Finally, it can be concluded that using the suggested method, ZnO and MgO nanoparticles in the ranges of 25-50 and 30-60 nm, respectively were synthesized. Also particle size about 65 nm with more spongy morphology was obtained for ZnO/MgO nanocomposite.

The XRD patterns of three samples of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite have been shown that all the peaks can be indexed to the known Wurtzite structure of ZnO and MgO powders and ZnO/MgO nanocomposite. No impurity such as $Zn(CH_3COO)_2$, $Zn(OH)_2$, $Mg(CH_3COO)_2$ and $Mg(OH)_2$ was detected. On comparison with standard XRD cards, the 2θ peaks observed at these patterns show hexagonal and cubic structures of ZnO and MgO, respectively. Peak broadening indicate crystallites smallness in nanometer scale. The average sizes of the particles are in good agreement with those observed from SEM images.

The FT-IR spectra of the ZnO and MgO nano-powder samples and commercial their powders have been shown that the absorbance characteristic of our high purity ZnO and MgO nanoparticles in comparison with commercial powders. In addition to this, the formed ZnO and MgO phases are characterized by intense and very broad IR band which could be assigned to the Zn-O and Mg-O vibrations with poor resolved shoulders at about 500cm^{-1}[23].

Finally, it can be concluded that while the suggested method is used, ZnO and MgO nanostructured and ZnO/MgO nanocomposite can be synthesized in nanometer scales. In this method, the presence of ultrasonic waves and structure director additive has strong positive effect on the morphology of the final products.

To application of nanopowders, three different zinc phosphate dental cements were prepared by combining the same powder formulation (TABLE 1) with the three different ratios of powder/liquid (gr/gr) of (1) 0.50:0.70, (2) 0.50:0.60 and (3) 0.50:0.40 (TABLE 2). Then various amounts of Harvard's liquid zinc phosphate dental cement were slowly added to the mixtrure and mixed for 1-2 min. The mixtures were heated to 1050°C in the furnace for 5 h. The premixed paste was placed into a mold of 6 mm diameter and 12mm depth, and sandwiched between two porous glass slides (ACE Glass, Vineland, NJ). The mechanical strength magnitude of 6mm diameter and 12mm thickness cement specimens were measured on a computer controlled universal testing machine with crosshead speed of 1 mm/min. It was founded when the ratio of powder/liquid was increased, the mechanical strength magnitude of cements also increased. However, by increasing the powder, the compressive strength of zinc phosphate cement prepared from the ZnO and MgO nano-powders were increased. In the ratio of 0.50:0.40 powder/liquid (3) maximum mechanical strength magnitude was observed. In the ratios higher than 0.60:0.40, the powder is insoluble. Therefore, this ratio was selected as the optimum value. In contrast to the conventional Harvard zinc phosphate cements, the ZnO and MgO nanostructured and ZnO/MgO nanocomposite cements were shown more increased mechanical strength magnitude. In the case of zinc phosphate cement the mechanical strength magnitude were varied from 11.44 N/mm^2 for available commercial sample of Harvard to 27.46 and 20.35 N/mm^2 for the obtained ZnO and MgO nano-powders and ZnO/MgO nanocomposite, respectively. Furthermore, the setting time of the prepared

TABLE 2 : Compressive strength values of commercial and formed zinc phosphate dental cements. The results are averaged values. Sample 1 is commercial zinc phosphate cement of Harvard, containing commercial ZnO and MgO powders. Samples 2, 3 and 4 are three prepared zinc phosphate cements in the present study, containing synthesized nanopowders

No.	Powder: Liquid (gr/gr)	Strength (N/mm^2)
1	0.75/0.50	59.08[a], 48.16[b]
2	0.60/0.70	74.40[a], 66.31[b]
3	0.50/0.60	79.53[a], 73.16[b]
4	0.50/0.40	42.73

[a]averaged values of compressive strength for ZnO and MgO nanostructured. [b]averaged values of compressive strength for ZnO/MgO nanocomposite

dental cement from ZnO and MgO nano-powders was assessed 2.5 to 4.5 min, which is acceptable and comparable to those obtained by commercial samples.

CONCLUSION

ZnO and MgO nanoparticles and ZnO/MgO nanocomposite were successfully prepared from $Zn(CH_3COO)_2$ and $Mg(CH_3COO)_2$ and elemental elemental chalcogenes using TMAH solution and PVP (0.1 M) as structure director additive. The results obtained in the present study show that the sonochemical method has proved to be simple and efficient. The uniform small sizes of ZnO and MgO nanostructured and ZnO/MgO nanocomposite can be used as active material in dental cements. The zinc phosphate dental cements obtained by synthesized nano-scale powders revealed excellent mechanical strength. This study showed that mechanical strength of dental cements is dependent on composition size scale. It was found that zinc phosphate dental cement had higher strength than conventional Harvard ZPC. The simplicity and low cost of the process would be favorable to high strength zinc phosphate dental cement, and this method may be developed to synthesize other effectiveness dental cements.

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