RESEARCH PAPER

Synthesis and Characterisation of Zein-Coated Magnesium Oxide (zMgO) Nano-Gel

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ABSTRACT

This pioneering research achieved a breakthrough in the field of zein-based metal oxide (MO) gels with the development of a biocompatible zein-coated magnesium oxide (zMgO) nanoparticle (NP) gel, offering a promising avenue for integration into medical devices and highly efficient drug delivery systems. The research methodology comprised synthesising ultrafine MgO NPs with a zein coating and gel preparations at varying concentrations. The resulting materials were extensively characterised using Fourier-transform infrared spectroscopy (FTIR), atomic force scanning electron microscopy (AF-SEM), energy-dispersive X-ray (EDX) mapping, and water contact angle (WCA) measurements. The findings from AF-SEM and EDX mapping revealed a uniform and consistent material dispersion, and WCA measurements indicated a hydrophilic surface characteristic. Additionally, FTIR spectra analysis suggested the absence of unforeseen interactions or the formation of new compounds during the synthesis process or in conjunction with zein. In conclusion, this study introduces a groundbreaking development in the form of zein-coated MO gels known for their biocompatibility. These innovative nanostructures have enormous potential for medical applications and the design of efficient and safe drug delivery systems, promising both effectiveness and safety in various medical, dental contexts.

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INTRODUCTION

Nanotechnology involves the synthesis, characterisation, and application of nanomaterials. A nanoparticle (NP) is an arrangement of atoms and molecules of several single or multiple elements on a nanoscale that range from one to one hundred nanometres (nm) [1]. The most significant metal oxides (MOs) are silicon dioxide, zinc oxide, ferric oxide, magnesium oxide (MgO), and titanium dioxide. These materials can be used in industries such as medicine, agriculture, information technology, electronics, energy, and environmental protection, as they possess unique features [2]. Recently, the application of nanomaterials as carrier materials to enhance the osteointegration in implant screws was carried out using eggshells as bone grafts around commercial pure titanium implant screws coated with nano calcium sulphate [3]. With modern implantology, fine and fast osseointegration is a significant factor influencing the success of dental implantation, and it largely depends on the implant surface

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coating comprising nanomaterials such as nano-hydroxyapatite and magnesium chloride [4]. Magnesium (Mg) is an important cofactor in hundreds of enzymatic reactions, of which protein and nucleic acid synthesis, mitochondrial integrity, plasma membrane permeability, and cell cycle are crucial physiological functions. It has many medical applications in orthopaedic implants due to its biocompatibility, low weight, and low modulus of elasticity, making it physically and medically compatible with bone [5]. Magnesium oxide (MgO) plays a critical role in bone regeneration and has recently shown promise in tumour treatment, expanding its applications beyond its traditional use as an antacid [6]. Magnesium oxide (MgO) variants, such as NPs, have demonstrated moderate bactericidal activity, significantly influenced by particle size and concentration. These MgO NPs are relatively insoluble and tend to form agglomerates [7]. The chemical structure of Magnesium oxide (MgO) consists of a magnesium cation (Mg2+) and an oxide anion (O2-), with its ultrafine nanoparticles in a size range between 1 and 100 nm forming a crystal lattice structure as shown in the [8]. And have demonstrated antibacterial activities mainly through releasing ROS and damaging bacterial cell membranes. There are several approaches to create magnesium oxide nanoparticles, including the sol-gel process, co-precipitation, and laser ablation [9]. One of the most popular methods is the sol-gel approach (MgO NPs). In the simplest sol-gel procedure, a precursor such as sodium hydroxide is added to a magnesium-based precursor such as magnesium nitrate ($MgNO_3.6H_2O$) to create a magnesium hydroxide gel or precipitate, followed by filtration, and calcination/annealing [10]. The uniform and effective heating process of the sol-gel synthesis is mainly mediated using microwave, providing an even distribution and greater surface area of particle size and requires less time than other irradiation techniques. To optimise the properties of MgO, using an appropriate surfactant-based stabiliser prevents agglomeration and aids in their dissolution.

Zein is a composite protein or polypeptide comprised of various proteins, classifiable based on solubility, charges, and molecular weights. The three primary fractions identified are α-zein, β-zein, and ɣ-zein, with molecular weights and solubilities distinguishing them [11]. The predominant fraction in corn's zein is α-zein, constituting 75–85% of the total, while β-zein and ɣ-zein account for 10–15% and 5–10%, respectively, depending on the genotype. α-zein exhibits a molecular weight between 21 and 25 kDa, with a minor subfraction at 10 kDa.

In contrast to β-zein and ɣ-zein, which necessitate reducing agents and/or buffers for dissolution, α-zein demonstrates solubility in alcohols ranging from 50 to 95 percent, without the requirement of additional reducing agents or buffers. The solvent that yielded the highest solubility for entire zein, considering all component fractions, was a 70% ethanol-aqueous solution employed for the extraction of α-zein from dry-milled maize [12].

Zein, a natural alcohol-soluble protein found in the endosperm tissue of corn, exhibits distinctive characteristics, such as biocompatibility and biodegradability. These qualities position the polymer as a prospective choice for creating micro or nanospheres and film coatings to enhance gene delivery [13]. Zein has extensive pharmaceutical applications, particularly in sugar-coating tablets, owing to its remarkable resistance to heat, humidity, and abrasion and its ability to mask strong odors and undesirable tastes.

Furthermore, due to its water-insolubility and swelling characteristics, zein has been investigated for its potential to regulate or prolong the release of drugs from various dosage forms [14]. Magnesium oxide (MgO) NPs can be easily created using several techniques. The sol-gel method is often one of the most popular methods of producing MgO NPs. In the simplest sol-gel method, a precursor, such as sodium hydroxide (NaOH), is added to an Mg-based precursor, such as magnesium nitrate, to create a magnesium hydroxide gel or precipitate. Once this has been filtered, a calcination or annealing process is conducted [15]. Applying a zein coating has notably impacted the physicochemical attributes of MgO. The inclusion of zein polymer in the formulation of MgO NPs results in a protective coating that effectively prevents the agglomeration of NPs. This polymer's inherent characteristics play a pivotal role in stabilising the particles against aggregation by reducing their hydrophobic properties [16].

Considering the cost and easy availability of these two materials, the goal of this research was to prepare zein-coated MgO (zMgO) NP gels of varying concentrations: 0.5%,1.0%, and 1.5%, and characterise them using Fourier-transform

infrared spectroscopy (FTIR), atomic force scanning electron microscopy (AF-SEM), energy-dispersive X-ray (EDX) mapping, and water contact angle (WCA) tests.

MATERIALS AND METHODS

Synthesising the Magnesium Oxide Nanoparticles (MgO NPs)

For synthesis, magnesium acetate tetrahydrate and citric acid were employed as the precursor and gelling agent, respectively, and were used in an equimolar combination. Initially, the precursor and the gelling agent were individually dissolved in ethanol and agitated using a magnetic stirrer for one hour. Subsequently, the solutions were mixed and subjected to ultrasonication at a constant frequency of 60 Hz, forming a pure white gel. The ultrasonication process was carried out for varying time intervals within the range of five to fifteen minutes.

The gel was left to age for 12 hours, followed by drying in a hot air oven at 100°C for another 12 hours. The dried sol-gel product was then ground to obtain a fine powder. Additionally, ultrasonication was incorporated into the sol-gel method to reduce the size of the sol-gel product before the calcination process [17].

Synthesising the Zein Nanoparticles (NPs)

To prepare the NPs, a solution containing 600 mg of zein and 100 mg of lysine was initially dissolved in a 70 mL mixture of ethanol and water in a 1:1 ratio by volume, with magnetic stirring at room temperature. Subsequently, the NPs were formed by continuously adding 700 mL of distilled water.

The resulting suspension was then subjected to purification and concentration through ultrafiltration using filter paper with a pore size of 0.15. Lastly, 20 mL of an aqueous mannitol solution was introduced to the zein NPs suspension, and the mixture was dried at room temperature overnight [18].

Encapsulating and Stabilising the Zein-coated Magnesium Oxide Nanoparticles (zMgO NPs)

Approximately 0.02 g of zein was weighed and dissolved in a mixture of ethanol and a 0.1 NaOH solution, with the ethanol making up 93.7% of the volume. Another solution was prepared, containing about 0.02 g of MgO and polyvinyl alcohol at a concentration of 0.9% (w/v). This second solution underwent ultrasonication, and the zein solution was slowly added drop by drop. An ice bath was employed to maintain a controlled temperature of 10°C in the aqueous phase.

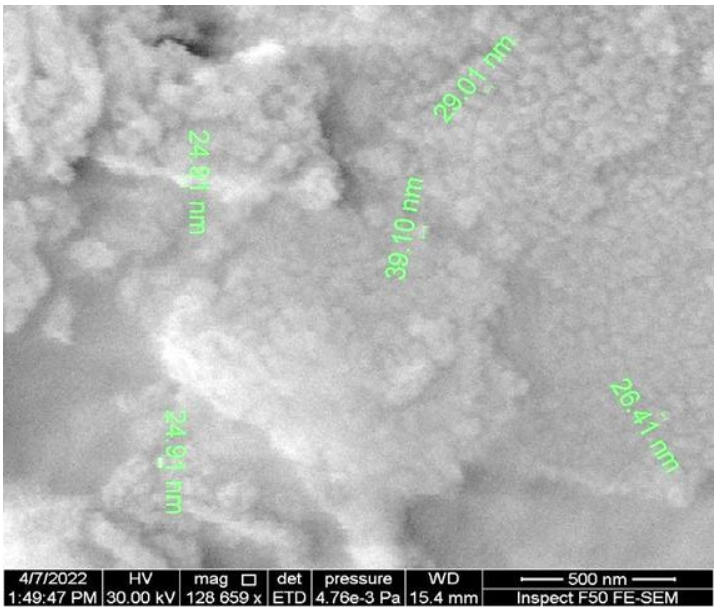

Fig. 1. Field emission Scan Electron Microscope of MgO nano powder.

Subsequently, the zMgO suspension was continuously stirred at 500 rpm to facilitate ethanol evaporation. To further purify the aqueous suspension of zein NPs, two cycles of differential centrifugation were used at 3000 rpm for 45 minutes each. The resulting mixture was then left to evaporate at room temperature overnight [19].

Preparing Different Concentrations of the Zein-coated Magnesium Oxide Nanoparticle (zMgO NP) Gels

Polylactic acid and gelatine were dissolved in NaOH solution and stirred continuously overnight to achieve a uniform solution, where the ratio of polylactic acid to gelatine was 8:2 (w/w), and the NaOH concentration was maintained at 10% (w/v) [20]. Following this, various amounts of zMgO: 0%, 0.5%, 1.0%, and 1.5% of the total volume (wt/v) were introduced into the solution and then thoroughly dispersed by subjecting the mixture to 30 minutes of sonication, resulting in the formation of the gel materials.

RESULTS AND DISCUSSION

Field emission SEM (FESEM) enables the direct examination of morphological and structural characteristics in particle samples. EF-SEM for the MgO nano powder showed that the maximum range of MgO nano powder was 39.1nm while the minimum range was 24.91nm (Fig. 1). The maximum range of Zein nanopowder was 39.1 nm and the minimum range was 33.98 nm (Fig. 2). The zMgO nano powder exhibited maximum and minimum ranges at 76.50 nm and 42.49 nm (Fig. 3). In this research, examining FESEM images reveals that zMgO exists at a nanoscale dimension and exhibits a consistent, even distribution in crystalline configuration. This uniform dispersion signifies the stability of the MO against potential factors that could alter its state. These findings are consistent with prior reports, as scanning and transmission electron microscopy images illustrate noticeably reduced aggregation of zMgO NPs while retaining their nano-sized structure, in contrast to pure MgO NPs [21].

The FTIR technique was employed to investigate the bonding characteristics of the materials. Spectra were recorded over a range from 4000 to 40 cm-1, and the stretching vibration of Mg-O bonds was observed below 600 cm-1. In the FTIR spectrum of zein, typical protein bands were evident. The band related to the stretching of N-H and O-H bonds in the amino acids appeared within the range of 2800 to 3500 cm−1, known as amide A. Another band at 1650 cm−1 corresponded to the carbonyl (C=O) stretching in amide groups of peptide structures (amide I). Additionally, the band at 1157 cm−1 was attributed to the axial deformation vibrations of the C-N bond. However, no bond alterations were present in the FTIR

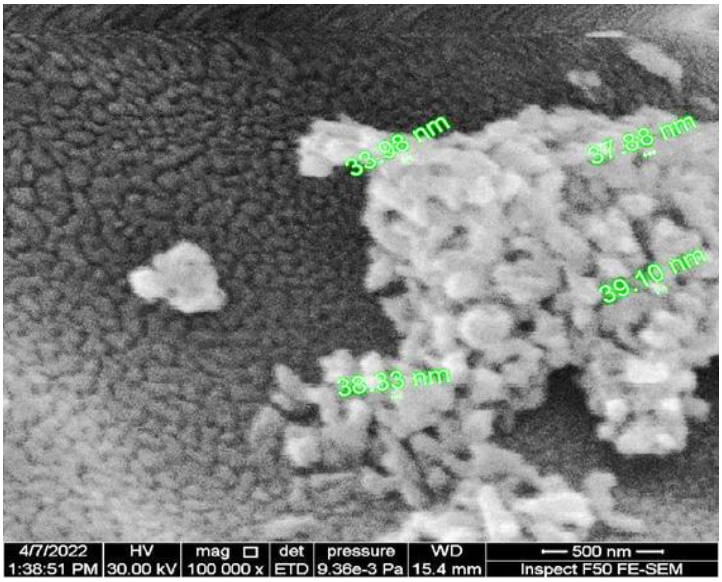

Fig. 2. EF-SEM for Zien nano powder.

spectrum of zMgO NP powder, as observed in Fig. 4..

In the FTIR spectra of the zMgO nanopowder, clear and distinct bands were observed, corresponding to the bridging hydrogen-bonded hydroxyl group present in zein and MgO. This hydrogen bond plays a crucial role in maintaining the stability of zein coatings around the MO

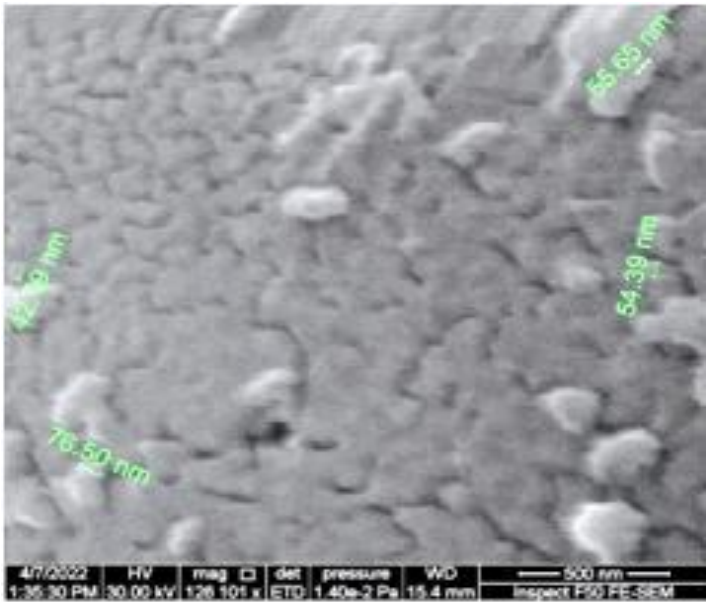

Fig. 3. The AF-SEM results of the zMgO NP powder.

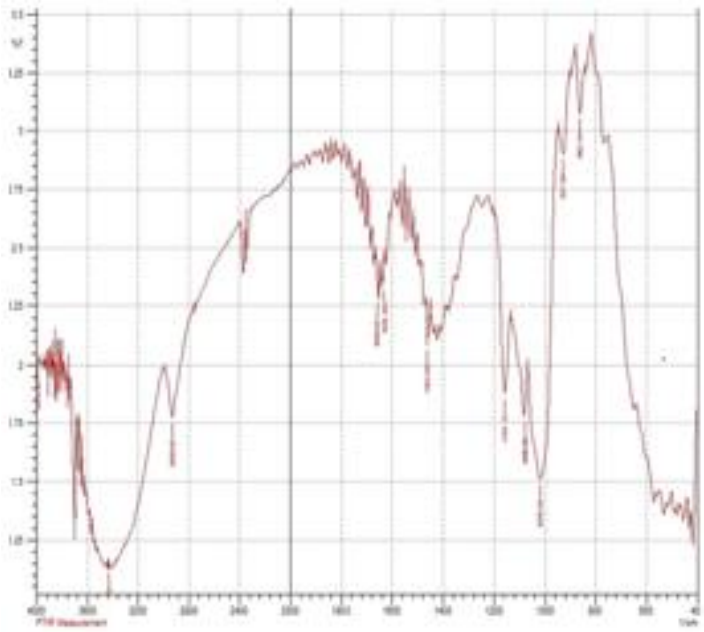

Fig. 4. The FTIR spectrum of the zMgO NPs.

nanopowder. The spectra displayed well-defined peaks, signifying the absence of any potential interaction or formation of new products during the synthesis process or in conjunction with zein. These results align with findings from previous studies on similar hybrid materials [22; 23]. In this context, the analysis of the zMgO gel at three different concentrations consistently yielded results that indicate a homogeneous and well-dispersed nature of the material.

The EDX of the 0.5%, 1.0%, and 1.5% gels provides elemental identification and quantitative compositional information for different concentrations, revealing an increase in the MgO concentration with the other elements.

EDX mapping of the zMgO shows a homogenous distribution of the compound materials Fig. 5. While the EDX of the 0.5%, 1.0%, and 1.5% gels are shown in Tables 1, 2, and 3, respectively, revealing their elemental concentrations.

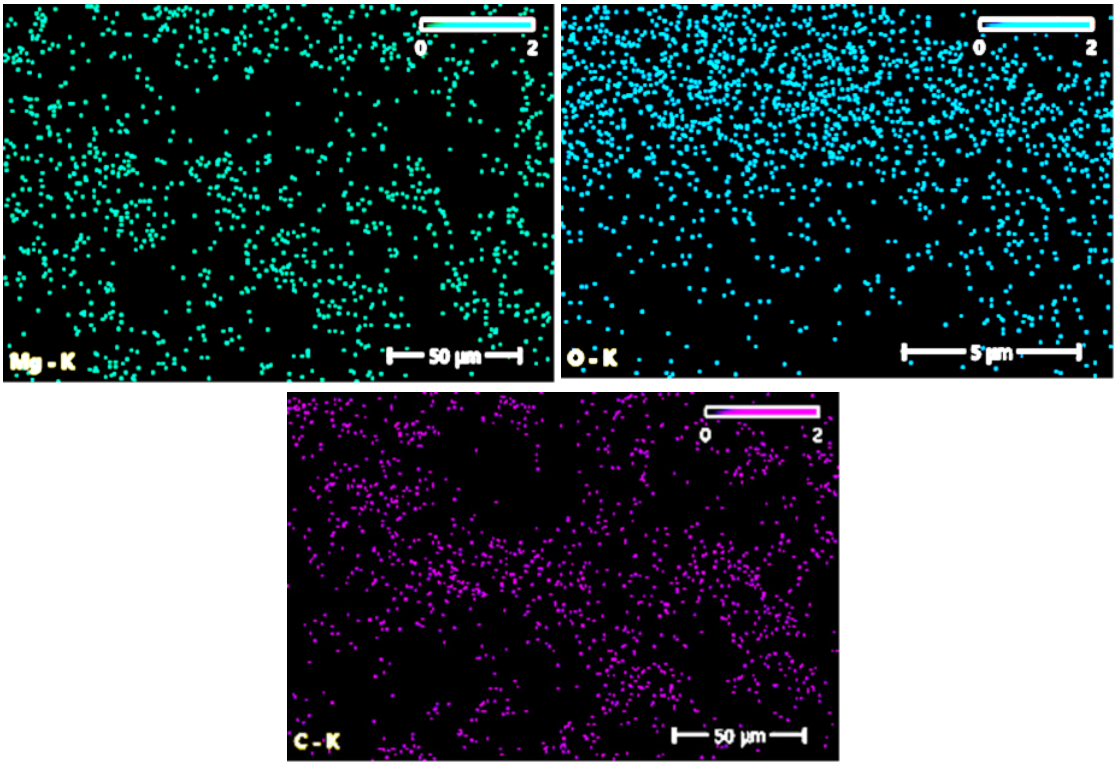

Fig. 5. EDX mapping for zMgO nanopowder.

Table 1. EDX of the 0.5% gel.

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	21.7	0.7	15.5	0.5
N	2.2	0.8	1.8	0.6
O	54.0	0.8	51.2	0.8
Mg	17.1	0.3	24.7	0.5
Cl	0.1	0.1	0.1	0.1

Table 2. EDX of the 1.0% gel.

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	25.4	1.3	16.0	0.9
N	2.2	1.7	1.9	1.4
O	54.7	2.0	51.2	1.9
Mg	25.8	0.8	25.8	1.1
Cl	0.1	0.1	0.0	0.1

Table 3. EDX of the 1.5% gel.

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	27.5	1.1	11.6	0.8
N	0.6	0.6	0.5	0.5
O	60.2	1.7	56.1	1.6
Mg	33.0	0.7	26.9	1.0

Table 4. The descriptive statistics of the samples' wettability.

Test	groups	Mean	SD	Maximum	Minimum
water contact angle test	0.5%	35.6	1.6733	38	34
	1%	23.6	1.6733	26	22
	1.5%	21.6	1.6733	24	20

To evaluate the wettability of the samples, their WCAs were determined by measuring their static WCAs with a goniometer. Table 1.4 presents the results of WCA measurements, including the mean, standard deviations, minimum and maximum values, as well as the *p* of all three concentrations; 0.5%, 1.0%, and 1.5%. A notable decrease in WCA was observed, indicating an increase in wettability particularly that of the 1.5% gel.

The WCA measurements for the 0.5%, 1.0%, and 1.5% gels revealed substantial and statistically significant variations. The 1.5% concentration had the lowest mean WCA (21.6 ± 1.67). A decrease in the mean corresponded to a shallower angle (< 90^o), indicating a hydrophilic surface character. This alteration can be attributed to the introduction of zein, yielding advantageous outcomes that agree with Li (2010), where the presence of adsorbed zein on nanostructured MgO amplifies the surface's wettability. The high surface area of MgO enhances MgO capacity in solvents, so there is a more uniform and homogeneous powdered composition [24].

CONCLUSION

The current study introduced a novel generation of MO gel. Incorporating zein, an extract derived from corn, in the MgO coating improved physicochemical properties. Zein-coated MgO NPs encapsulated within a gel matrix exhibit biocompatibility. Our future outlook encompasses utilising zein as a stabilising agent for various MOs and investigating potential biological interactions. Furthermore, the prospective exploration of these new hybrid materials, including zMgO, holds promising prospects within the medical domain, from biological applications to optimising their physical properties for diverse applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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