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Mesoporous silica nanoparticles supported copper(II) and nickel(II) Schiff base complexes: Synthesis, characterization, antibacterial activity and enzyme immobilization

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ABSTRACT

Mesoporous silica nanoparticles (MSNs) were prepared by sol-gel method and functionalized with 3-aminopropyltriethoxysilane. Schiff base grafted mesoporous silica nanoparticle was synthesized by the condensation of 2-hydroxy-3-methoxybenzaldehyde and amine-functionalized MSNs. The latter material was then treated with Cu(II) and Ni(II) salts separately to obtain copper and nickel complexes anchored mesoporous composites. The newly prepared hybrid organic-inorganic nanocomposites have been characterized by several techniques such as FT-IR, LA-XRD, FE-SEM, TEM, EDS, BET and TGA. The results showed all samples have MCM-41 type ordered mesoporous structure and functionalization occurs mainly inside the mesopore channel. The presence of all elements in synthesized nanocomposites and the coordination of Schiff base via imine nitrogen and phenolate oxygen were confirmed. MSNs and all functionalized MSNs have uniform spherical nanoparticles with a mean diameter less than 100 nm. The as-synthesized mesoporous nanocomposites were investigated for antibacterial activity against Gram-positive (*B. subtilis* and *S. aureus*) and Gram-negative (*E. coli* and *P. aeruginosa*) bacteria, as carrier for gentamicin and also for immobilization of DNase, coagulase and amylase enzymes. MSN-SB-Ni indicated bacteriocidal effect against *S.aureus* and all compounds were found to be good carrier for gentamicin. Results of enzyme immobilization for DNase and coagulase and α-amylase revealed that supported metal complexes efficiently immobilized enzymes.

1. Introduction

Nanomaterials are the subject of intense research worldwide due to their unique physical and chemical properties as well as potential biomedical applications. Over the past two decades, synthetic routes to numerous nanoparticles with different compositions and properties and diverse range of chemical and biological applications have been developed [1–6]. Among many nanosized materials, mesoporous silica nanoparticles (MSNs) are important because of the interesting structural features and the potential applications.

According to the International Union of Pure and Applied Chemistry (IUPAC), a mesoporous material is defined as a porous material with pore diameters between 2 and 50 nm. Mesoporous silica materials are important composites because of their wide applications in various fields [7–10]. These materials have unique properties such as high surface area, chemical, thermal and mechanical stability, narrow suitable channels as well as the ability of surface modification by active silanol groups. Mesoporous materials are applied for catalysis, immobilization of enzymes and proteins, photocatalysis in solar cells, fuel cells and batteries, pollutant remediation and drug delivery [11–17]. Based on the synthesis method and directing agent template, various mesoporous silica compounds have been fabricated and categorized as M41S, SBA, MSU, etc [18]. M41S family is included MCM-41, MCM-50 and MCM-48 and among them, MCM-41 is the most widely studied mesoporous silica [19–21]. Mesoporous silica nanoparticles (MSNs) are a type of MCM-41 that have particle sizes under 100 nm with interesting properties such as biocompatibility, controllable particle size or shape and have other features of MCM-41 [22–25]. Among different inorganic nanoparticles, MSNs have gained specific importance as new generation systems for drug delivery [26–28]. Bulk mesoporous silica materials with micrometer size are not suitable to be used in drug delivery systems because of their rapid settlement in solutions. The solution suspendability of MSNs is an important factor for biomedical application as nano-carriers [22]. More

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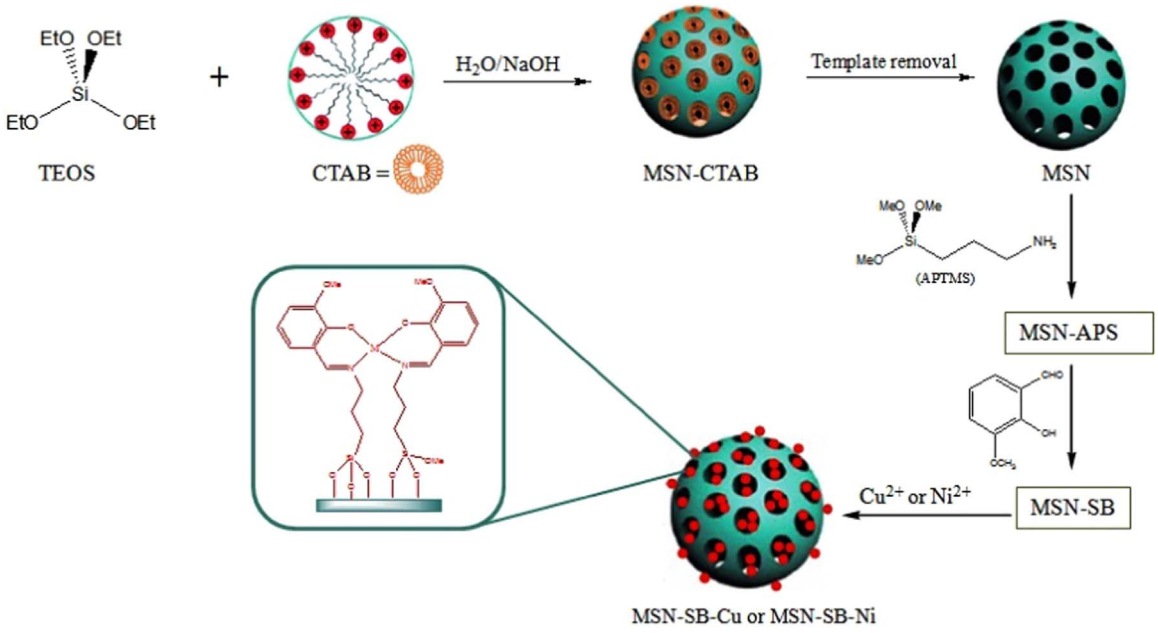

Fig. 1. The route for synthesis of the functionalized MSNs.

often these nanoparticles have been employed as catalyst for different organic reactions such as epoxidation of alkenes, conversion of CO_2 to heterocyclic compounds, polymerization and etc. MSNs have been shown to be better catalysts than either graphen oxide or MOFs in respect of high yields and stability [29–31]. The pore size of mesoporous silica materials is suitable for accommodating small molecules or enzymes. Considering the importance of biocatalysts in nanotechnology, mesoporous materials as support for immobilization and amplification stability of enzymes have been explored extensively during the last two decades. Mesoporous silica nanoparticles with suitable and ordered pores and solution suspendability overcome some limitations of the other mesoporous materials, MCM-41 and SBA-15, and therefore they are very promising candidates for enzyme immobilization in recent years [28,32,33]. Immobilized enzymes were also used for biosensing, biofuels and drug delivery [34–39]. Enzyme immobilization on mesoporous silica can be performed through physical adsorption or chemical interaction [40,41].

In the present research work, a Schiff base and its Ni(II) and Cu(II) complexes have been prepared and supported on MSNs. In view of the wide applications of Schiff bases and their complexes and the unique properties of MSNs, these hybrid composites were designed to provide suitable surface for efficient interaction with drugs and enzymes. Copper and nickel complexes by having low toxic, good biological activity and extensive application as biocatalyst centers looks suitable candidates for this propose [42,43]. The antibacterial activity of the synthesized materials as well as their capability for gentamicin adsorption and enzyme (DNase, coagulase and α-amylase) immobilization were investigated.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), hexadecyltrimethyl ammonium bromide (CTAB, 99%), 3-aminopropyl trimethoxy silane (APTMS, 95%), sodium hydroxide, 2-hydroxy-3-methoxy benzaldehyde ($C_8H_8O_3$), $Cu(OAc)_2{\cdot}H_2O$, $Ni(OAc)_2{\cdot}4H_2O$ and ethanol purchased from Merck chemical company. Ultrapure water was obtained from Millipore pure water system. All chemicals were of analytical-reagent grade and used without further purification.

2.2. Characterization methods

Morphology and dimensions of nanoparticles were determined by a field emission scanning electron microscope (FE-SEM) equipped with EDS analyzer model Mira 3-XMU and with an accelerating voltage of 15 kv. Transmission electron microscopy (TEM) images were obtained on a Zeiss - EM10C microscope with an accelerating voltage of 80 kv. A small angle powder X-ray diffraction data were collected by a XRD apparatus model X Pert Pro using CuKα irradiation at 40 kv and 30 mA. Fourier transform infrared spectra (FT-IR) were recorded by a FT BOMEM MB102 spectrophotometer in the range of 400–4000 cm^{-1} using the KBr discs. Thermogravimetric analysis (TGA) of the samples were carried out using a STA 1500 thermal analyzer at a heating rate of 10 °C min^{-1} and temperature range of 0–850 °C. N_2 adsorption-desorption isotherms were obtained at liquid N_2 temperature on a Belsorp mini II apparatus. Samples were degassed at 130 °C for 15 h prior to analysis. The surface area was calculated by Brunauer-Emmet-Teller (BET) method, and pore size distribution was estimated from the adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. Measurement of absorption for evaluation of antibacterial activity has been fulfilled by eliza reader model Bio-rad 680 Microplate Reader.

2.3. Synthesis of mesoporous silica nanoparticles (MSNs)

A mixture of CTAB (1 g), deionized water (480 mL) and NaOH (3.5 mL, 2 M) was stirred at 80 °C. TEOS (5 mL) was slowly added to this solution. A milky gel was formed after 2–3 min and stirred at 80 °C for 2 h. Then the gel was filtered, washed several times with ethanol and water and dried in oven overnight. For the extraction of CTAB, the solid was dispersed in an ethanolic solution (100 mL) of concentrated HCl (2 mL), refluxed for 24 h and then filtered and dried in oven at 80 °C.

2.4. Synthesis of amine-functionalized MSNs (MSN-APS)

APTMS (1 mL) was added to the synthesized MSN (0.1 g) dispersed in ethanol (50 mL) and this mixture was refluxed under N_2 atmosphere for 3 h. A white precipitate (MSN-APS) was formed, which was filtered,