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Short communication

Effect of bio-template on the properties of SiO_2/Al_2O_3 composites for drug delivery

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ABSTRACT

In this study, SiO_2/Al_2O_3 composites (C-SLNs) were successfully synthesized using chitosan as the template for drug delivery. The C-SLNs had higher specific surface areas (244–607 m^2/g), total pore volumes (0.19–0.34 $cm^3\,g^{-1}$), and narrow mesopore size distribution. The porosity of the C-SLNs prepared under high Si/Al ratio conditions was achieved mostly by the formation of wider pores that were distributed in the meso-/macro-pores. And, the C-SLNs were used as a levofloxacin carrier to study its drug release behavior, which exhibited an initial fast release followed by a sustained release and antibacterial effectiveness over a long period.

Introduction

Currently, the development of new, efficient, environmentally safe, cheap, and biodegradable slow/controlled release materials as drug carrier materials in agricultural and pharmaceutical industries is a major challenge. This is particularly important because the innovations and benefits afforded by these delivery systems suggest that developmental focus in this direction will remain to be active for many years to come. However, there are two factors restricting this process. Firstly, ensuring the sustained/controlled release performance of products is a challenge and secondly, the cost of production and ensure that the product is environmentally safe are pertinent issues [1,2].

To date, many different materials have been used as drug carrier materials including polymers (PPC, PVC, PVP, chitosan, etc.), silica, zinc oxide (ZnO), calcium carbonate ($CaCO_3$), and several others [3–7]. In particular, silica nanomaterials have a high potential for application in many areas including as adsorbents, photonics, catalysts, sensors, superhydrophobic surfaces, polymer fillers, and a host of other fields [8–10]. Mesoporous silica has made very significant progress in the past decades as a very important silica nanomaterial in scientific research. This is because of its good biocompatibility, higher specific surface area, adjustable pore size distribution, and the ease of surface modification with different organic groups [11–13]. Furthermore, mixed oxides have attracted more research interest than pure oxides because they have larger specific surface area, higher chemical stability, higher surface acid, and mechanical strength. Among the various mixed oxides, the SiO_2/Al_2O_3 mixed oxides, particularly, the mesoporous form, have shown excellent properties including chemical stability, easy availability, reusability, and easy-to-design pore structure [14–16].

Recently, various templates and methods have been developed to improve the morphology, specific surface area, and porosity including the synthesis of mesoporous silica-based nanoparticles. Although different methods have been used to prepare SiO_2/Al_2O_3, the sol–gel process is one of best because it controls the morphology of the final materials with a high purity and specificity. Various templates have been used as surfactant in the synthesis of mesoporous materials [17–19].

In particular, chitosan, which is a linear nontoxic bio-polymer with high adsorption properties due to it the presence of hydroxyl and amino groups has been used for this purpose [20,21]. The functional groups present in chitosan make it an excellent candidate to produce hybrid organic–inorganic composite sol–gels, as templates in the presence of acidic oxides. Rajarajeswari et al. [20] used chitosan as a template to synthesize a mesoporous nanotitania photocatalyst. Kadib et al. [22] prepared porous metal oxide microspheres with filamentary nanoparticles using chitosan as a template. Sifontes et al. [23] prepared cerium oxide nanoparticles using chitosan as a template, cerium nitrate as a starting material, and sodium hydroxide as a precipitating agent. Therefore, we proposed that sol–gel synthesis of SiO_2/Al_2O_3 using

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chitosan as a template and mesoporous silica-based materials would yield a higher specific surface area. In this study, chitosan was used as a bio-template to prepare mesoporous SiO_2/Al_2O_3 composite particles for drug delivery, in an attempt to reduce the cost of raw materials by using environmentally safe and renewable resources.

Materials and methods

Sample preparation

SiO_2/Al_2O_3 composites were prepared according to the following three steps. Firstly, a mixture of tetraethyl orthosilicate (TEOS, 5.6 mL), ethanol (C_2H_5OH, 8.7 mL), aluminum nitrate ($Al(NO_3)_3$, 0.75 g, Si/Al = 50), and hydrochloric acid (HCl 0.01 M, 2.7 mL) was stirred at 40 °C for 1 h. The different chitosan/silica ratios ($m_{chitosan}/m_{chitosan\ +\ silica}$ = 0.1 (11.5 mL), 0.2 (25.5 mL), 0.3 (43.5 mL), and 0.4 (68 mL); chitosan molecular weight, M_w, 10,000, 1.2 wt%) were dissolved in an acidic solution (2 wt% aqueous acetic acid) and then slowly added to the original TEOS mixture with vigorous stirring at 40 °C for 30 min. The gel obtained was air dried at 25 °C for 5 days in a mold. The transparent composite film was calcined at 550 °C for 2 h. The resultant samples were designated as *G-n*, where *n* is the ratio of $m_{chitosan}/m_{chitosan\ +\ silica}$ (0.1, 0.2, 0.3, and 0.4). To determine the effect of varying the aluminum content on the pore structure of the C-SLNs, different proportions of $Al(NO_3)_3$ were used to prepare a transparent composite gel following steps. A mixture of tetraethyl orthosilicate (TEOS, 5.6 mL), C_2H_5OH, (8.7 mL), $Al(NO_3)_3$ (Si/Al = 100 (1.5 g), 150 (2.25 g), and 200 (3 g)), and HCl (0.01 M, 2.7 mL) was stirred at 40 °C for 1 h. The 25.5 mL chitosan (1.2 wt%) were dissolved in an acidic solution (2 wt% aqueous acetic acid) and then slowly added to the 1.5 g TEOS mixture ($m_{chitosan}/m_{chitosan\ +\ silica}$ = 0.2) with vigorous stirring at room temperature for 30 min. The gel obtained was air dried at 25 °C for 5 days in a mold. The transparent composite film was calcined at 550 °C for 2 h. These samples were designated as *H-m*, where *m* is the ratio of Si/Al (100, 150, and 200). In vitro levofloxacin release from the obtained samples was investigated by soaking 10 mg of each material (SiO_2/Al_2O_3 composites loaded with drug) in 10 mL of a PBS (phosphate buffer solution, pH = 7.4), in dark conditions at 37 °C with continuous orbital stirring at 100 rpm for 48 h. The amount of levofloxacin released to the PBS was determined by UV spectrophotometry at 293 nm.

Characterization

Nitrogen (N_2) adsorption–desorption isotherms were measured using the gas adsorption technique (BET) on a surface area analyzer (Beckman Coulter, SA3100). The morphology of the nanofibers was observed using SEM with a scanning electron microscope (Hitachi S4500) and transmission electron microscopy (TEM, JEOL-2000-FX microscope). The ultraviolet (UV)–visible (Vis) spectra were recorded using a JH754 UV/Vis spectrophotometer (Jinghua Co.).

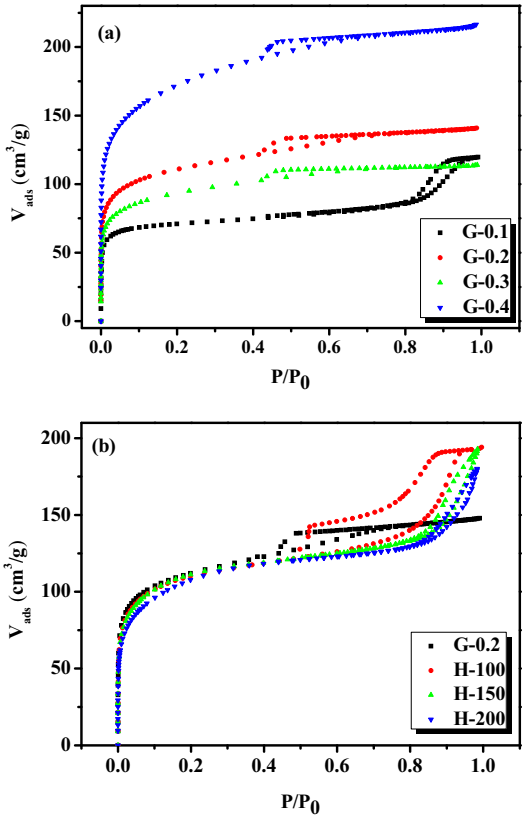

Fig. 1. Nitrogen (N_2)/77 K full isotherms of the silica/alumina (SiO_2/Al_2O_3) nanocomposites (C-SLNs). (a) G-0.1, G-0.2, G-0.3, and G-0.4 transparent film composites; and (b) H-50, H-100, H-150, and H-200 transparent composite gels.

Results and discussion

To confirm the pore structure of the C-SLNs, we used N_2/77 K isotherms, and the results are shown in Fig. 1(a). The adsorption data curves of the samples show that they are type-IV isotherms, according to the International Union of Pure and Applied Chemistry (IUPAC) classification. The comparison of all the sample curves shows that the chitosan template promoted the development of micro-/mesoporosity, by the air calcination of the template at 550 °C. The adsorption capacity increased significantly with increasing chitosan content. This suggests that samples produced with the chitosan template are composed mainly of mesopores. Fig. 1(b) shows the change in the shape of the isotherms (P/P_0 range, 0.4–1) with increasing Si/Al ratio from 50 to 200, indicating the main changes in the mesopore structure of the prepared C-SLNs. This suggests that samples produced at low Si/Al ratios are composed mainly of mesopores, and those synthesized at high chitosan/chitosan-silica (C/CS) ratios are composed mainly of micro/mesopores [20–24].

Table 1 provides the details of the textural properties of the prepared C-SLNs. The micropore, mesopore, and total pore

Table 1
Textural properties of the silica/alumina (SiO_2/Al_2O_3) composites (C-SLNs).

Sample	S_{BET} (m^2/g)	$S_{MicroBET}$ (m^2/g)	V_{Mi} (mL/g)	V_{Me} (mL/g)	V_T (mL/g)	V_{Me}/V_T (%)
G-0.1	244	188	0.085	0.105	0.190	55.3%
G-0.2	384	228	0.098	0.122	0.220	55.4%
G-0.3	431	247	0.101	0.149	0.250	59.6%
G-0.4	607	275	0.120	0.230	0.350	67.6%
H-100	389	214	0.094	0.206	0.300	69.0%
H-150	395	200	0.086	0.204	0.290	70.3%
H-200	385	146	0.061	0.219	0.280	78.2%