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Synthesis of bioactive polyvinyl alcohol/silica hybrid fibers for bone regeneration

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ABSTRACT

Polyvinyl alcohol/silica (PVA/SiO_2) hybrid fibers were prepared via a sol–gel combined electrospinning technique, and their potential application in bone tissue engineering was evaluated in terms of in vitro bioactivity. When the PVA concentration was 8%, the obtained PVA/SiO_2 hybrid fibers exhibited a uniform and continuous morphology, with an average fiber diameter of about 542.9 nm. The SiO_2 xerogel phase was uniformly distributed within the PVA matrix, and its actual content was very close to the theoretical value. After 3 days of immersion in simulated body fluid (SBF), the PVA/SiO_2 hybrid fibers displayed a vigorous precipitation of lamellar apatite crystals, reflecting their excellent in vitro bioactivity.

1. Introduction

Organic-inorganic hybrids have attracted considerable attention recently because they can combine effectively the advantages of both organic and inorganic components and tune their properties on the molecular and nanoscale levels [1–3]. Natural bone is a kind of organic–inorganic hybrid consisting of collagen fibers and hydroxyapatite crystals. By mimicking the structure of natural bone, various polymer-inorganic hybrid fibers have been developed for bone tissue engineering [4–6].

Polyvinyl alcohol (PVA), one of the intensively used polymeric biomaterials, possesses good biocompatibility, biodegradability, processability and water-solubility [7]. The hybrid of PVA with sol–gel derived silica which has gained increasing interest as a bioactive inorganic material can significantly improve the biological functions and mechanical properties of the PVA materials [2,8,9]. However, despite the above-mentioned potential benefits, there has been little research on formulating the PVA/SiO_2 hybrid into fibers for bone tissue regeneration so far.

This study is proposed to synthesize the bioactive PVA/SiO_2 hybrid fibers with a desirable morphology for bone tissue regeneration. Firstly, a spinnable PVA/SiO_2 hybrid sol was prepared in a pure aqueous medium, without any addition of alcohols. Subsequently, this hybrid sol was formulated into fibers via electrospinning. The composition and morphology of the as-prepared PVA/SiO_2 hybrid fibers were characterized by means of SEM, TEM, FT-IR and TG/DTA measurements, and the in vitro apatite-forming ability was investigated to evaluate their potential applications for bone tissue engineering.

2. Experimental procedure

Polyvinyl alcohol (PVA-124) powder (Aladdin Reagent Company, Shanghai, China) used in this study has an alcoholysis degree of 98.0–99.8% and an average polymerization degrees of 2400–2500. To prepare a suitable solution for electrospinning, the PVA powder was firstly dissolved in deionized water at 90 °C, and then a certain amount of tetraethyl orthosilicate (TEOS) and HCl (1 M) were slowly added into the PVA solution. After being fully stirred at room temperature, the mixture was incubated at 60 °C for 2 days to ensure the complete hydrolysis of TEOS, eventually generating a homogeneous PVA/SiO_2 hybrid sol with the theoretical SiO_2 content of 20 wt%. Subsequently, this hybrid sol was transferred into a glass syringe and then electrospun at a flow rate of 0.7 mL/h, an electric voltage of 20 kV and a collector distance of 10 cm. The as-spun fibrous membrane was stored in a desiccator to avoid the moisture absorption. For the bioactivity study, the hybrid fibers should be cross-linked so that they can maintain the fiber morphology in the aqueous solution. The glutaraldehyde (GA) solution as the cross-linking agent was prepared by diluting 50% aqueous

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GA with 0.5M Na_2SO_4 to 0.2M GA concentration, adjusted to pH 3.0 with 1M H_2SO_4 [10]. The PVA/SiO_2 hybrid fibers were immersed in the above GA solution at 80 °C for 24 h, after which the fibers were fully washed and then dried in air.

The morphology of the PVA/SiO_2 hybrid fibers was characterized by scanning electron microscope (SEM, FEI QuantaTM 250) and transmission electron microscopy (TEM, Tecnai G2 F20). The diameter distribution of the fibers was determined by measuring 250 individual fibers in the SEM images. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer 983G) was applied to identify chemical groups of the pure PVA and PVA/SiO_2 hybrid fibers. The thermal stability of the hybrid fibers was investigated by thermogravimetric-differential thermogravimetric analysis (TG-DTA, NETZSCH STA 409C). The in vitro bioactivity of the PVA/SiO_2 hybrid fibers was evaluated by immersing the fibrous membrane (1×1 cm^2) in 5 mL simulated body fluid (1.5SBF, pH 7.4) at 37 °C. After 3 days of immersion, the membrane was analyzed by SEM and X-ray diffraction (XRD, D8 Advance).

3. Results and discussion

This paper demonstrated a facile and green method to produce the PVA/SiO_2 hybrid fibers. A clear, viscous PVA/SiO_2 hybrid hydrosol was firstly obtained by in-situ hydrolysis of TEOS in the PVA solution, without the addition of any alcohol as the co-solvent. Afterwards, the hybrid sol was molded into continuous fibers via electrospinning. The effective combination of the sol–gel and electrospinning techniques can ensure the in-situ generation and homogenous dispersion of the SiO_2 xerogel in the PVA matrix [11,12], thus promisingly achieving the PVA/SiO_2 hybrid fibers with desirable biofunctions.

The morphology of the PVA/SiO_2 hybrid fibers was observed by SEM. The results indicated that the concentration of PVA had a great impact on the fiber morphology. Apparently, there were some droplets and beads existing in the fibers when the PVA concentration was less than 8%, as depicted in Fig. 1(a) and (b). It can be interpreted that the low PVA concentration made the viscosity of the spinning solution insufficient to form a uniform fiber. As the PVA concentration increased to 8%, droplets and beads disappeared and the hybrid fibers showed a uniform morphology, without obvious structural defects. However, a further increase of the PVA concentration to 9% led to some junctions between the hybrid fibers (Fig. 1(d)), which may be due to the high viscosity of the spinning precursor. In addition, it was also observed that the diameters of the PVA/SiO_2 hybrid fibers gradually increased with the increase of the PVA concentration. Based on the above results, the optimal concentration of PVA for preparing the PVA/SiO_2 hybrid fibers was determined as 8%. Thereafter, all the below-mentioned hybrid fibers were prepared at this condition.

The PVA/SiO_2 hybrid fibers shown in Fig. 1(c) exhibited a wide size distribution ranging from 150 to 900 nm, and the average fiber diameter was measured to be approximately 542.9 nm, as displayed in Fig. 2(a). The TEM observation was used to further investigate the inner structure of the PVA/SiO_2 hybrid fibers. The results revealed a dense and homogeneous microstructure without any crack or agglomeration, indicating the uniform hybrid of SiO_2 with PVA (Fig. 2(b)).

The FT-IR analysis was employed to investigate the formation and transformation of chemical structures during the preparation processes. As displayed in Fig. 3(a), the spectrum of pure PVA possessed strong absorption peaks located at 3362, 2924 and 1090 cm^{-1}, which were assigned to the stretching vibrations of the O—H, C—H and C—OH groups, respectively [13]. The hybrid of PVA with SiO_2 induced a red shift to 3296 cm^{-1} in the —OH stretching bands, implying the possible interaction between them. Moreover, the prominent absorption peaks of the Si—O—Si groups occurring at 1077, 834 and 464 cm^{-1} [14] confirmed the formation of SiO_2 within the hybrid fibers. In addition, the band corresponding to the Si—OH stretching mode was observed at 963 cm^{-1} due to the incomplete polycondensation of silica, which were frequently observed in many sol–gel derived materials [15].

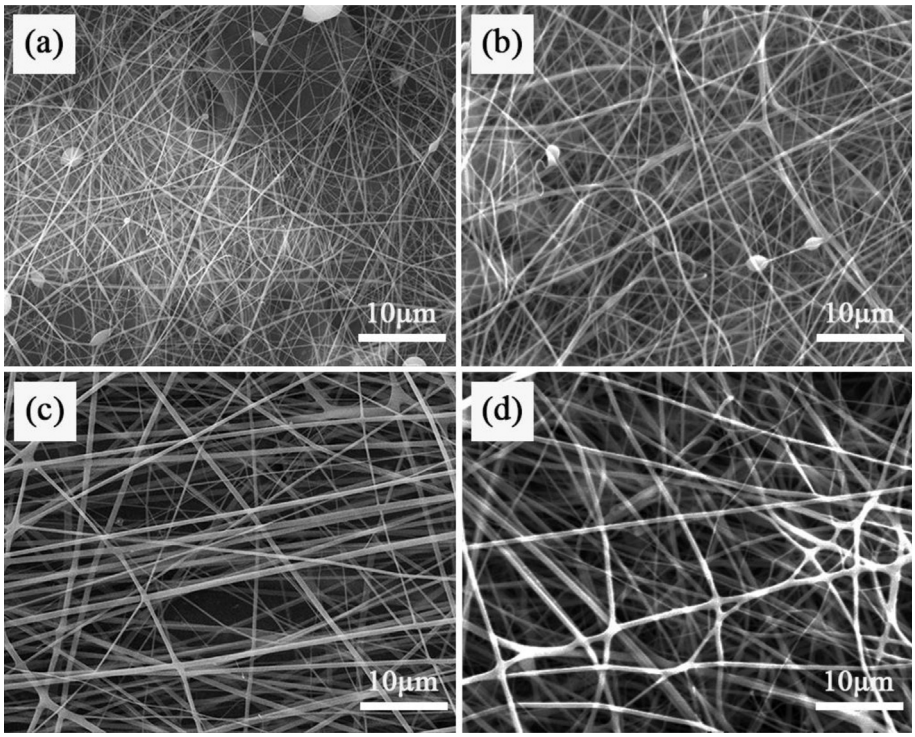

Fig. 1. SEM images of the PVA/SiO_2 hybrid fibers prepared at different PVA concentrations: (a) 6%; (b) 7%; (c) 8%; (d) 9%.