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Short communication

Chondroitin sulphate-guided construction of polypyrrole nanoarchitectures

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ABSTRACT

Nanospheres, nanocones, and nanowires are three typical polypyrrole (PPy) nanoarchitectures and electrochemically polymerized with the dope of chondroitin sulphate (CS) in this study. CS, a functional biomacromolecule, guides the formation of PPy nanoarchitectures as the dopant and morphology-directing agent. Combined with our previous reported other PPy nanoarchitectures (such as nanotube arrays and nanowires), this work further proposed the novel mechanism of the construction of PPy/CS nanoarchitectures with the synergistic effect of CS molecular chains structure and the steric hindrance. Compared to the undoped PPy, MC3T3-E1 cells with PPy/CS nanoarchitectures possessed stronger proliferation and osteogenic differentiation capability. This suggests that PPy/CS nanoarchitectures have appropriate biocompatibility. Altogether, the nanoarchitectured PPy/CS may find application in the regeneration of bone defect.

1. Introduction

Studies have suggested that diabetes mellitus (DM) may increase osteoclastogenesis by inhibiting endochondral bone formation and cause bone loss and nonunion [1–4]. Therefore, a number of diabetic patients with bone fracture have been healed delay. The electrical stimulation has been used as a bone treatment method widely [5–7], in which the functional component is the conductive materials [8]. Therefore, conducting polymers, especially nanoarchitectured conducting polymers with fine conductivity have been increasingly explored for the application of bone tissue engineering. Herein, a novel formation of chondroitin sulphate (CS) doped adjustable nanoarchitectured PPy as the medium for electrical stimulation transport was investigated for the potential application in the regeneration of bone defect.

Nanoarchitectured CPs have the advantages of short transport path for ions, large surface area, and particularly conductivity. This may enhance the biological activity of protein adsorption, cell adhesion and proliferation. Additionally, it may be used in chemical/biological sensing, drug delivery, energy storage, and intelligent switching materials [9–11]. Up to date, the template techniques [12–14] and the template-free techniques [15–17] have mainly been employed to obtain nanoarchitectures of CPs. Although the template-based techniques are frequently used, the removal of template (e.g., anodic aluminum oxide and track-etched polycarbonate) may impair the nanoarchitectures due to the usage of strong acidic or basic medium. Through many years, a variety of strategies have been sought to achieve the nanoarchitectures without the use of templates. Interestingly, the biomolecule-assisted method in template-free techniques is mild, effective and environment-friendly. For instance, the specific biomolecules, containing DNA [18] and heparin [19], are capable of providing active sites in ordered pattern along the molecular chains in the fabrication of nanoarchitectures without external additive. Shi et al. have used heparin [19], starch [20] and hyaluronic acid (HA) as biomolecule dopants to assist the synthesis of PPy nanowires. They have proposed the biomolecules as dopants and morphology-directing agents assisting in the polymerization of one dimension (1 D) PPy nanowires.

CS with rich $-COO^-$ and $-SO_3^-$ functional groups on the chain, which is similar to heparin and HA, may be used to assist the synthesis of PPy nanoarchitectures. Moreover, CS is one of the major organic extracellular matrix components [21] and it has been reported that CS modulated essential proteins and precursor cells in the bone regeneration [22,23]. Additionally, PPy/CS incorporated PLA scaffolds by electrical stimuli affected the proliferation and osteogenic

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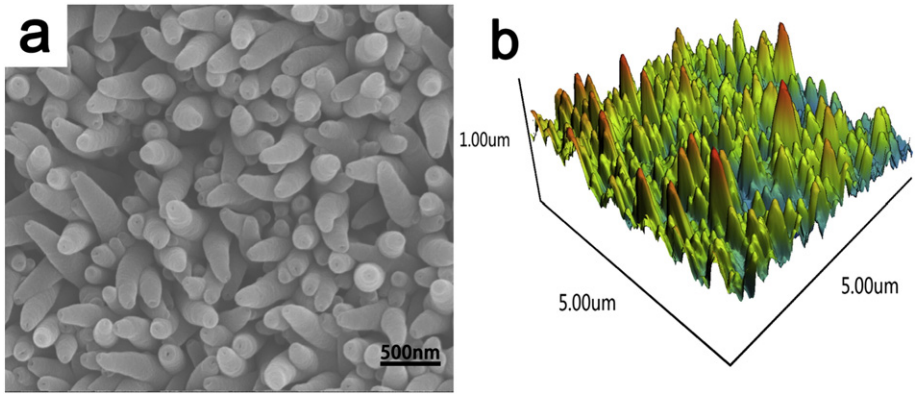

Fig. 1. PPy/CS nanocones fabrication. (a) SEM image of PPy nanocones. (b) AFM topography 3D image of PPy nanocones.

differentiation of stem cells [24]. PPy/CS also showed inducing mineralization capability on human adipose stem cells, which was greater than PPy-HA [25]. Therefore, the PPy/CS is associated with osteogenesis. However, whether the CS modulates the formation of nanoarchitectured PPy and its osteogenic property is still unclear. In this study, CS was used as a structure guiding-agent to fabricate morphological controllable PPy/CS nanoarchitectures on titanium substrate (nanospheres, nanocones and nanowires), and a potential mechanism of CS-guided construction of nanoarchitectured PPy was proposed. The CS molecular chains acted as templates which binded pyrrole (Py) monomers on the $-COO^-$ groups and $-SO_3^-$ groups through hydrogen bonds. PPy was formed preferentially along CS chains when the electrochemical polymerization was initiated. The PPy nanoshapes were constructed by the restricted space that was from the steric hindrance of CS, Py and the intermediate compounds. Furthermore, nanoarchitectured PPy/CS was involved in inducing the proliferation of MC3T3-E1 cells and the osteogenic differentiation compared to that of undoped PPy film without nanoarchitectures. This suggests that the nanoarchitectured PPy/CS has the potential in osteogenesis.

2. Materials and methods

2.1. Materials

Py and CS (99% purity) were purchased from Aladdin Chem Co., Ltd. (Shanghai, China). The inorganic salts for phosphate buffer saline (PBS) were of analytical grade and purchased from Guangzhou Chemical Reagent Co. Ltd. (Guangzhou, China). All of them were used without further purification. Titanium (Ti) sheets for biomedical application (0.2 mm thick) were obtained according to standard ASTM F67-2002 from Baoji Qichen New Material Technology Co., Ltd. The water used in this work was deionized water and the reaction was conducted at room temperature.

2.2. Synthesis of CS-doped PPy

The synthesis of PPy was similar to our previous work [26]. Briefly, the PPy coatings were synthesized on Ti sheet with effective area of 15 mm × 15 mm as working electrode. Ti sheets were rinsed prior to

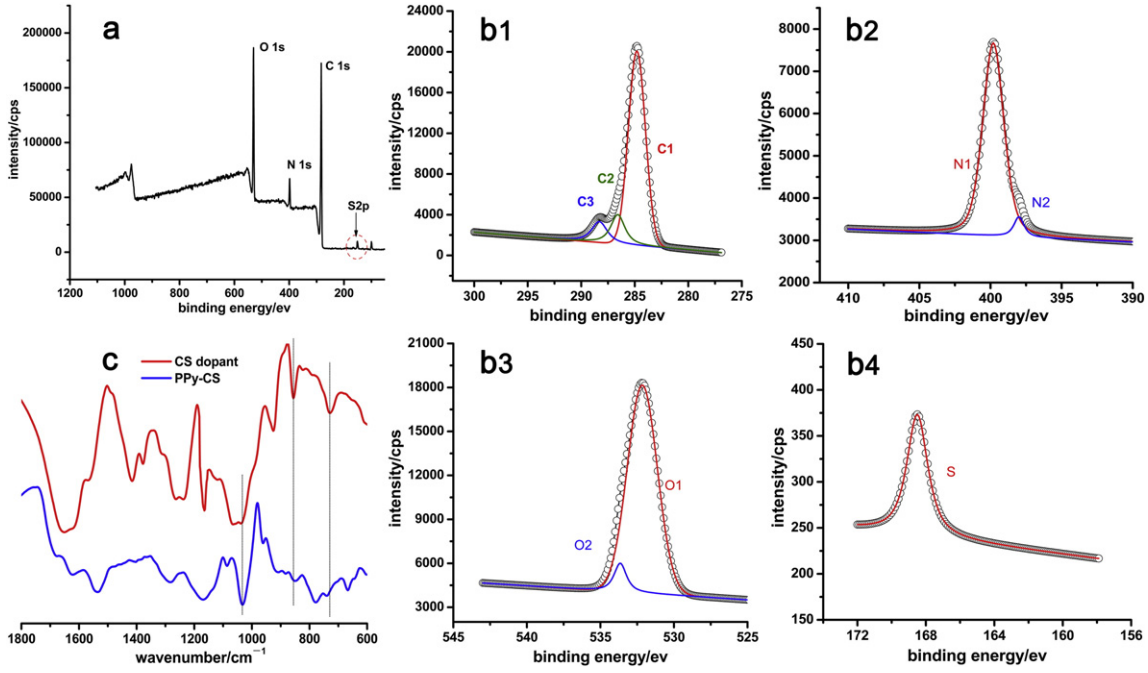

Fig. 2. PPy/CS nanocones characterizations. (a) XPS survey spectrum showing the elemental composition of PPy/CS. (b) Deconvoluted XPS C1s (b1), N1s (b2), O1s (b3) and S2p (b4) spectra of PPy/CS nanoarchitectures. (c) FTIR spectra of CS dopant and PPy/CS.