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Colloidal particle based electrodeposition coatings on NiTi alloy: Reduced releasing of nickel ions and improved biocompatibility

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ABSTRACT

Photo-crosslinking copolymer Poly (2-Hydroxyethyl methacrylate-*co*-2-(Dimethylamino) ethyl methacrylate-*co*-7-hydroxy-4-methylcoumarin methacrylate) (PHDC)) was first synthesized by free radical polymerization of 7-hydroxy-4-methylcoumarin methacrylate (CA), 2-Hydroxyethyl methacrylate (HEMA) and 2-(Dimethylamino)ethyl methacrylate (DMA). Then, the copolymers were self-assembled into colloidal particles and immobilized on the NiTi alloy by a simple one-step electrophoretic deposition. After irradiation, a photo-crosslinked coating was obtained. The structure and morphology were characterized by OCA and SEM. The copolymer coatings could significantly decrease the release of nickel ions into the environment and reduce cytotoxicity inducing by nickel ions according to immersion experiment. Meanwhile, the coatings have good cytocompatibility. This work provides a simpler polymer coating method to inhibit the release of toxic ions by inducing ion adsorption with certain molecular structures, which have potential for biomedical applications such as artificial bone and bone fixation device.

1. Introduction

Nickel-titanium memory alloys (NiTi alloys) have been widely used as excellent biomedical materials for orthopedics and interventional treatment materials due to their good resistance to fatigue and corrosion, light weight, and excellent mechanical properties being similar to bone, etc. [1,2]. In general, after the successful implantation of biomaterials, the impact on the body is a very complicated process reflecting in blood reactions, tissue reactions and immune reactions, and these biological reactions have an important significance in assessing their biocompatibility [3]. However, NiTi alloys generally contain 50% nickel. Once the alloy was implanted in the body, nickel ions in the NiTi alloys might gradually pits and releases. The enrichment and long-term presence of nickel ions in human body can cause many problems, such as cytotoxicity, tissue and organ disorders. [3–9] This problem need to be solved continuously in long-term clinical and experimental research.

In the continuous development of NiTi alloys biomaterials, the release of nickel from NiTi alloys can be effectively reduced by a certain surface treatment method, and one of the best methods is the coating treatment [10]. In previous studies, many surface modification methods such as sol–gel and plasma spraying were used for surface coating treatment which can effectively improve the corrosion resistance of the NiTi alloys, and greatly reduce the release of nickel ions, thereby significantly increase cytocompatibility [11]. In these systems, the processes are usually very complicated, expensive and multiple steps. Moreover, the coatings are typically fragile or biologically inert.

Herein, one simpler and controllable method, one-step electrodeposition of self-assembled colloidal particles, is used for preparing the nanostructure coating. The photo-crosslinked polymer coating could provide a more stable and dense surface for increasing the corrosion resistance of NiTi alloy [12]. And at a given polymer structure, the coating significantly reduces the release of nickel ions in the environment based on physical barriers and physical adsorption. This polymer coating also provides a novel toxic ion adsorption method and have good cytocompatibility, which have potential for biomedical applications such as artificial bone and bone fixation device.

2. Materials and methods

2.1. Synthesis of photosensitive copolymer

7-hydroxy-4-methylcoumarin methacrylate (CA) was synthesized according to literature [13]. The other reagents and solvents

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Table 1
Parameter of synthesized PHDC copolymer by ^{1}H NMR and GPC.

Sample	HEMA/DMA/CA feed	Actual ratio	Mn (g/mol)	PDI (Mw/Mn)
PHDC-1	10: 8: 2	10.2: 7.9: 2	1.64×10^4	1.36
PHDC-2	8: 10: 2	8.1: 10.5: 2	1.46×10^4	1.41

were purchased from Aladdin (shanghai, China). 2-Hydroxyethyl methacrylate (HEMA), 2-(Dimethylamino) ethyl methacrylate (DMA) and CA were dissolved in 90 mL Dioxane with a 200 mL polymerization tube using azobisisobutyronitrile (AIBN) (1 mM) as the initiator. After deoxygenation, the sealed tube was immersed into an oil bath by magnetic stirring at 70 °C. After 24 h, the photosensitive PHDC with different contents was obtained by precipitation third into petroleum ether and vacuum drying. The ^{1}H NMR (400 MHz, DMSO d_6) and gel permeation chromatography (THF, HPLC) were used to investigate the structure and properties of copolymers, the monomer theoretical ratio, actual ratio, molecular weight (Mn) and distribution (PDI) of these polymers are shown in Table 1.

2.2. Self-assembly of copolymers

The copolymers PHDC was dissolved in dioxane (20 mL). Under stirring, substantial ultrapure water (60 mL) was added rapidly. After stirring for 4 h, then dioxane was removed by dialysis against deionized water for 3 d. The final PHDC colloidal particles solutions were obtained. The PHDC nanoparticle morphologies and size distribution were determined by transmission electron microscope (TEM, 200 kV) and ZetaPALS particle size analyzer, respectively.

2.3. Preparation of photo-crosslinked coating

The NiTi alloys plates (composition: 51 wt% Ni, Φ3×1 × 0.2 cm, Baoji Xilian Tianium Industry Co., Ltd) were immersed in 4.0 mg/mL PHDC colloidal particles solution as cathode, and a platinum plate was used as anode. The uncrosslinked nanostructured coating (un-NiTi-CP) was fabricated on NiTi alloys by electrodeposition with a constant voltage of 15 V for 5 min. Then, the photo-crosslinked coating was fabricated (NiTi-CP) by irradiation of an area UV curing system (1000 W) for 10 min. Surface properties of coating were measured by scanning electron microscopy (SEM, 2.0 kV) and optical contact angle measuring device (OCA).

2.4. Immersion experiment

Sterilized bare NiTi alloys and NiTi-CP were immersed in 30 mL simulated body fluid (SBF) respectively. [14] The immersion extracts (10 mL) were collected from these solutions at 1, 5, 10, 20 and 30 days, then 10 mL fresh SBF were was supplemented immediately. The immersion extracts were used for detecting the cumulative release of Ni^{2+} using flame atomic absorption spectrometry and used for culture cells.

2.5. Biocompatibility study

Cytocompatibility was investigated with NIH-3T3 cells. The immersion extracts (10%/v: v) were added into culture media for evaluating the effect of nickel ion release on cell viability. NIH-3T3 cells were directly seeded onto the test samples in 6-well plates at a density of 6×10^3 cells per well and evaluated the

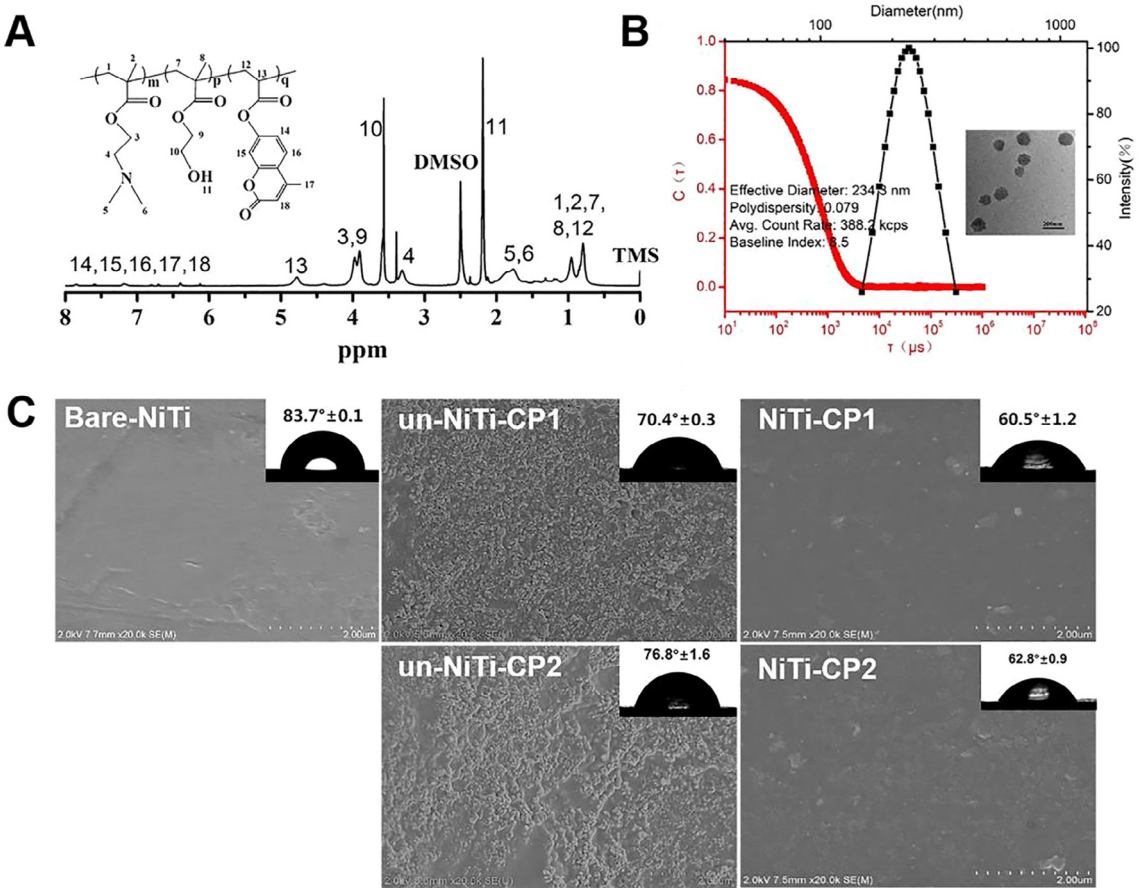

Fig. 1. ^{1}H NMR spectrum of copolymer PHDC-1 (A); size, morphology (B) of PHDC-1 colloidal particles; SEM images and OCA images of coatings (C).