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Polymeric Nanoparticles Based Multi-Functional Coatings on NiTi Alloy with Nickel Ion Release Control, Cytocompatibility and Antibacterial Performance

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1. Copolymer section

Materials

7-hydroxy-4-methylcoumarin methacrylate (CA) was synthesized according to literature. 2-hydroxyethyl methacrylate (HEMA, 96%), 2-(dimethylamino) ethyl methacrylate (DMAEMA, 99%), 1-bromododecane and azobisisobutyronitrile (AIBN, recrystallized, 99%) were purchased from Aladdin (shanghai, China). HEMA and DMAEMA was purified by passing through basic alumina columns to remove the inhibitor. All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

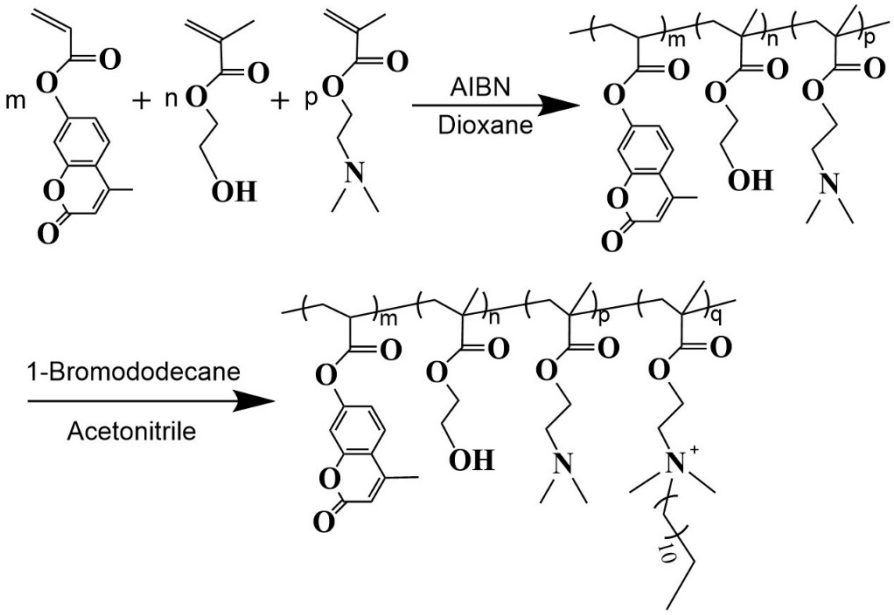

Figure S1. Schematic diagram of copolymer PCHD and quaternized copolymer PCHD-Q.

Synthesis of photosensitive copolymer PCHD

The copolymers with different contents (1:5:4 and 1:4:5, meaning mole ratio of CA, HEMA and DMA units), were fabricated by a typical radical polymerization, and denoted as PCHD1 and PCHD2 respectively (Figure S1). A typical synthesis procedure of PCHD-1 was as follows: CA (1.09 g, 5 mmol), HEMA (3.25 g, 25 mmol) and DMAEMA (3.14 g, 20 mmol) was added into a 250 mL polymerization tube and dissolved in 90 mL Dioxane at a room temperature using AIBN (0.164 g, 1

mmol) as the initiator. After the polymerization tube was passed into nitrogen 30 min to remove oxygen, then the sealed polymerization tube was immersed into an oil bath by magnetic stirring at 65 °C. After 24 h, the reaction mixture was purified by precipitation three times into an excess amount of petroleum ether. Finally, the obtained PCHD1 was dried overnight under vacuum at 25 °C. PCHD2 was obtained by the similar method.

Synthesis of quaternized copolymer PCHD-Q

The synthetic route of copolymer PCHD-Q was also shown in Figure S1. The photosensitive copolymers PCHD (2 g) was added into a 50 mL polymerization tube and dissolved in 20 mL acetonitrile at a room temperature, then 1-bromododecane with different amounts (0.036 g and 0.36 g) was added to the mixture. The sealed polymerization tube was immersed into an oil bath by magnetic stirring at 70 °C. After 24 h, the reaction mixture was purified by precipitation three times into an excess amount of diethyl ether. Finally, quaternized polymers were obtained by vacuum drying at 25 °C, and marked as PCHD-Q1 and PCHD-Q10 respectively.

Taking PCHD1, PCHD1-Q1 and PCHD1-Q10 for instance, the ^{1}H-NMR spectrum (Bruker MSL-300, $CDCl_3$, δ, ppm) is investigated the structure of quaternized copolymers PCHD1-Q1 and PCHD1-Q10, and all peaks confirm the chemical formation of the copolymer, as shown in Figure S2. According to the spectrum of PCHD1, the peaks δ of 6.1-7.9, 4.8 and 2.5 ppm assigned as the hydrogen protons of conjugated rings of CA segments at the 13, 14,15,16,17,18, respectively. The peak at δ=3.9, 3.6 and 2.1 ppm are ascribed to the proton at 9, 10 and 11 of HEMA segments, respectively. The peak δ of 4.0, 3.3 and 1.8 ppm is the proton of the DMA at 3, 4, 5 and 6, respectively. This shows that the copolymer PCHD1 was successfully prepared. And the peak areas at δ = 6-8, 3.6 and 3.33 were used for calculating the reality ratio of CA, HEMA and DMA that is 2: 10.2: 7.9. For quaternary ammonium salt group, new peaks at δ = 3.1 and 1.3 arose in the ^{1}H NMR spectrum, which

were assigned to the quaternary ammonium groups at 19 and 20, respectively. The intensity of the proton peaks is significantly enhanced as the degree of quaternization increases from 1% to 10%. The results confirmed that PCHD1-Q1 and PCHD1-Q10 copolymers were synthesized successfully. In addition, Mn and PDI of PCHD1, PCHD1-Q1 and PCHD1-Q10 was determined by GPC.

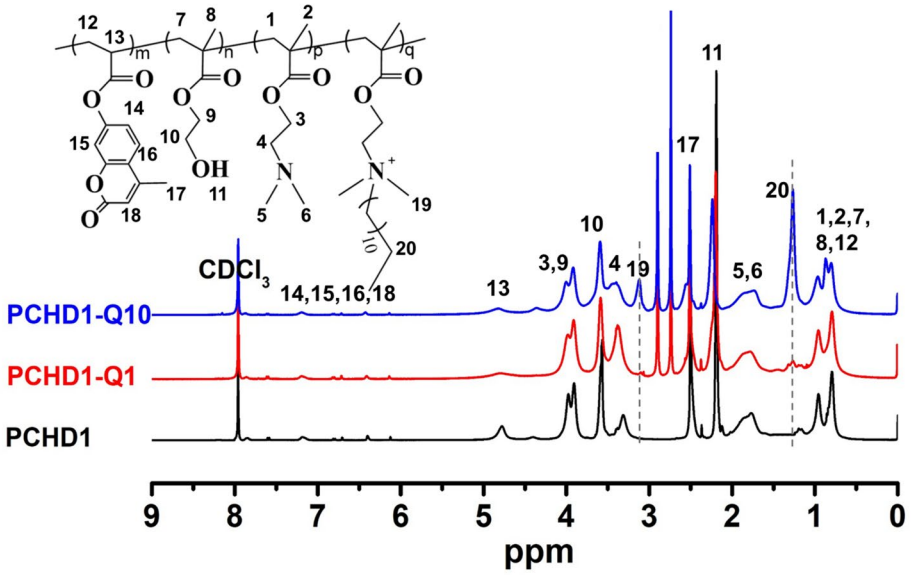

Figure S2. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrums of quaternized copolymer PCHD1, PCHD1-Q1 and PCHD1-Q10 copolymer.

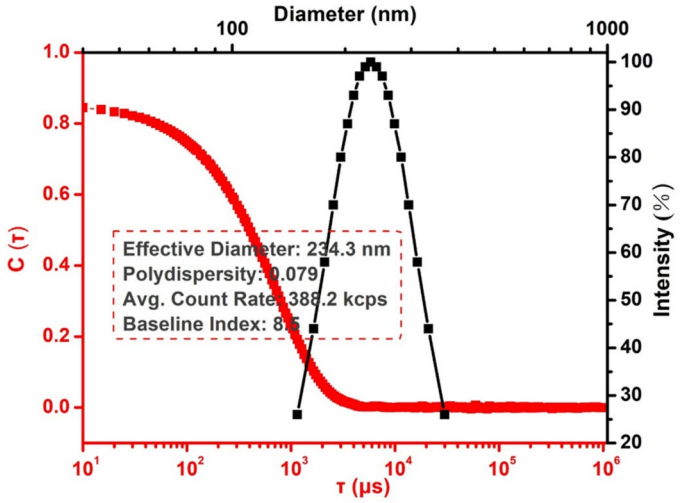

Figure S3. Average particle sizes and size distributions of PCHD1 nanoparticles.

2. Preparation of copolymer coatings on the NiTi substrates

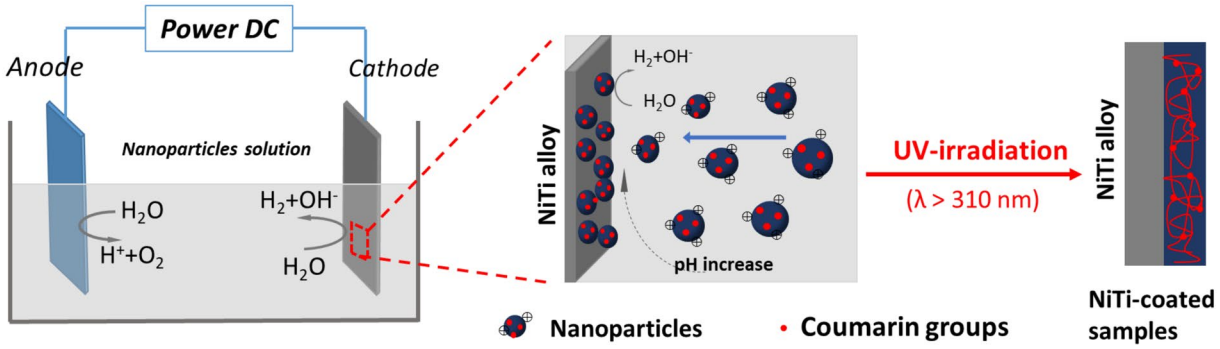

Figure S4. Illustration of electrodeposition of nanoparticles on NiTi alloy.

The copolymer contained many tertiary amine or quaternary ammonium salt groups, the self-assembled nanoparticles are positively charged. As positively charged particles, we fabricated coating materials on the NiTi alloy by utilizing cathodic electrodeposition. The electrodeposition process is described as follows: Under the applied electric field, the positively charged nanoparticles were derived and migrated to the cathode (NiTi alloy) surface, and this migration also could induce a concentration gradient of colloidal particle around the NiTi alloy surface. In the process of migration to the cathode surface (NiTi alloy), the nanoparticles surface started deprotonation leading to a drop in surface charge with increasing pH value (cathode reactions: $H_2O \rightarrow H^+ + OH^-$, $2H^+ + 2e^- \rightarrow H_2$). Then the electrolyte system became flocculation, dissolved out and deposited on NITi alloy surface. After 5 min with 15 V deposition voltage, the initial coatings were formed as a result of continuous accumulation of nanoparticles. After that, the initial coating was photochemically dimerize via direct UV irradiation ($\lambda > 310$ nm). After 10 min, the photo-cross-linked coating samples were obtained.

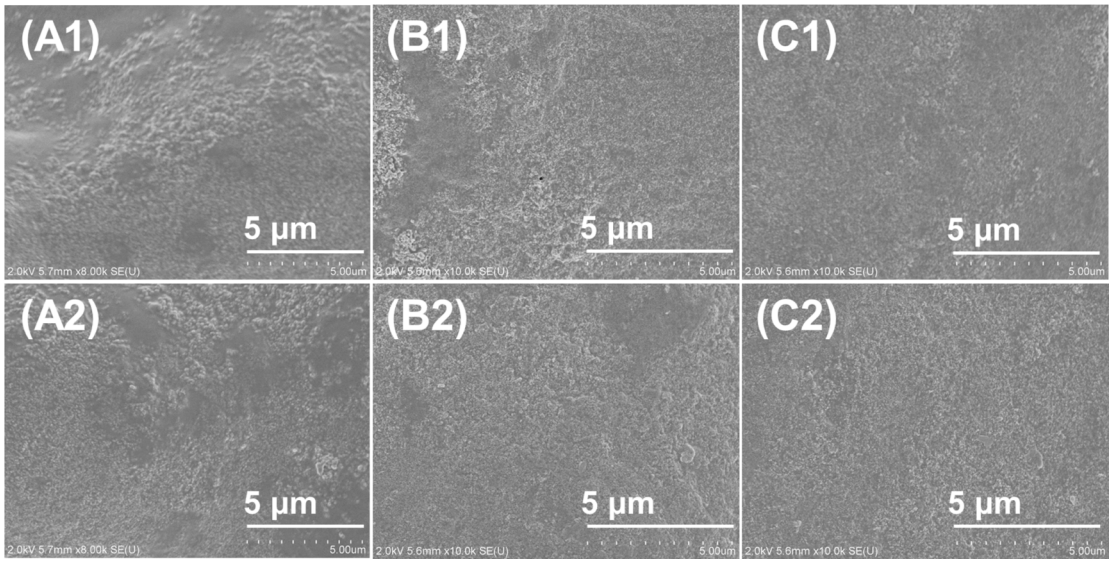

Figure S5. SEM images of the NiTi-PCHD1 (A1), NiTi-PCHD1-Q1 (B1), NiTi-PCHD1-Q10 (C1), NiTi-PCHD2 (A2), NiTi-PCHD2-Q1 (B2) and NiTi-PCHD2-Q10 (C2) before photo-cross-linking.

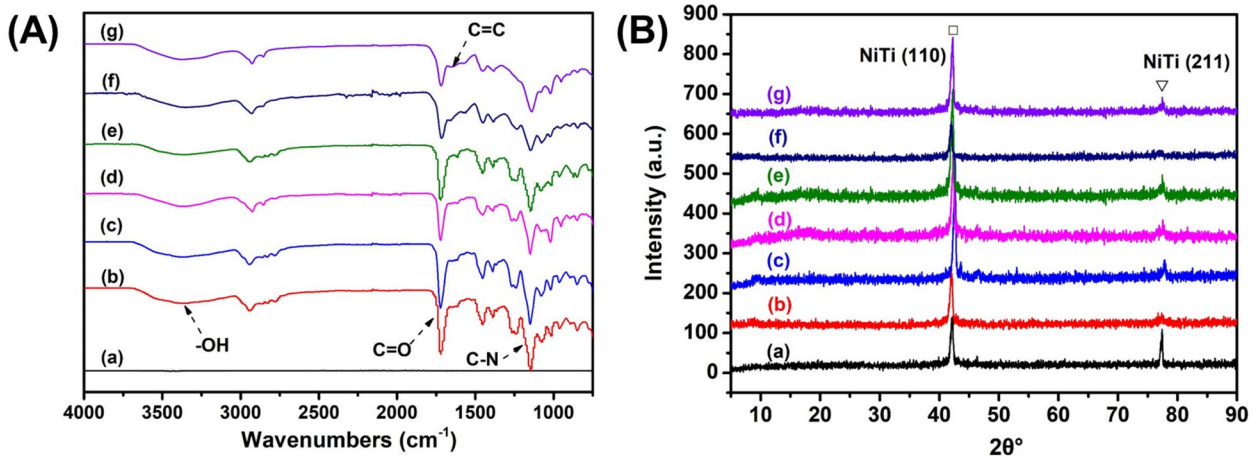

Figure S6. The FTIR spectra (A) and XRD pattern (B) of the bare NiTi (a), NiTi-PCHD1 (b), NiTi-PCHD1-Q1 (c), NiTi-PCHD1-Q10 (d), NiTi-PCHD2 (e), NiTi-PCHD2-Q1 (f) and NiTi-PCHD1-Q10.

3. Immersion experiment *in vitro*

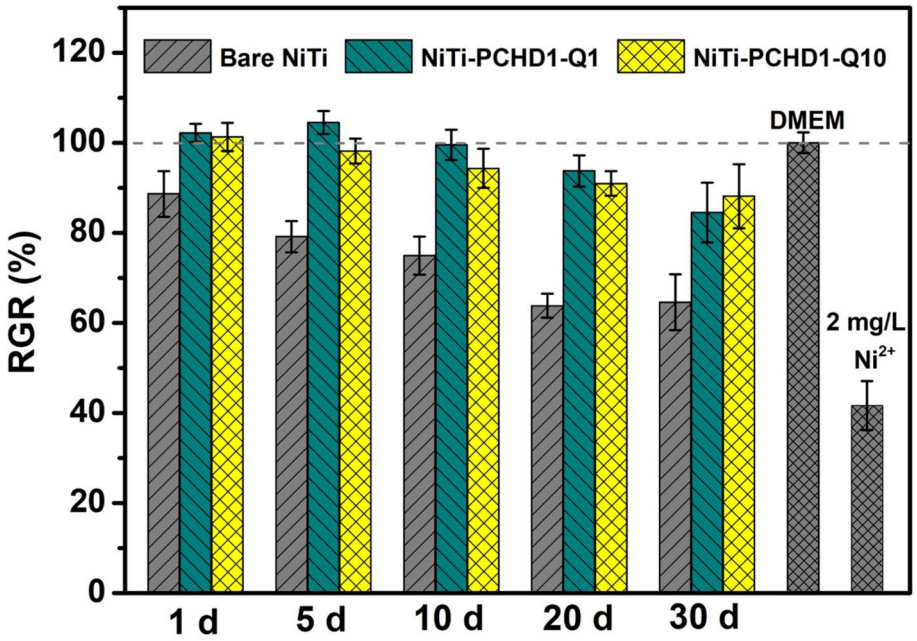

Figure S7. Cell morphology viability of NIH-3T3 cells after culturing for 48 h with different immersion extracts of Bare NiTi, NiTi-PCHD1-Q1 and NiTi-PCHD1-Q10, the DMEM and Ni^{2+} of 2 mg/L samples as controls.

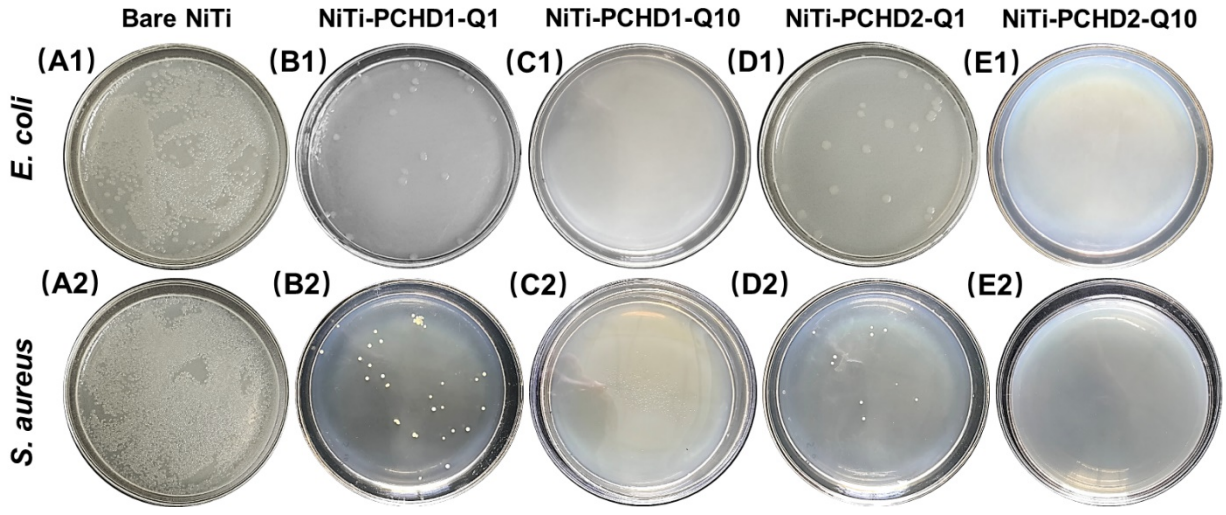

Figure S8. Plate count tests of *E. coli* (A1-E1) and *S. aureus* (A2-E2) from different coatings for 24 h incubation.