Supporting Information

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Table of Contents

1. General
2. NMR results of PVA-TP-COOH and PVA-TP-CA
3. Synthesis of metal-incorporated PVA-TP-CA coating
4. Scanning electron microscopy (SEM)
5. X-ray Photoelectron Spectroscopy (XPS)
6. Water contact angle measurement
7. Antibacterial activity
8. Atomic force microscopy (AFM)
9. *In vitro* Co^{II} ions release experiments
10. Cell culture study
11. Immunocytochemistry
12. MSC differentiation and alkaline phosphatase (ALP) staining and quantification
13. Cell viability assays
14. Statistical analysis

References
1. General

All reagents were commercially available and used as supplied without further purification. Compounds PVA-COOH\textsuperscript{S1} and TP\textsuperscript{S2} were prepared according to the published procedures. Dialysis was performed in benzyolated cellulose tubes (D7884, 32 mm width, molecular weight cut-off (MWCO) 2000 g\textcdot mol\textsuperscript{-1}) from Sigma–Aldrich Munich, Germany. The deionized water used was purified using a Millipore water purification system with a minimum resistivity of 18.0 MΩ\textcdot cm. NMR spectra were recorded on a Bruker ECX 400 MHz spectrometer. Confocal laser scanning microscopic investigations were done on a TCS SP8, Leica, Germany. UV-vis spectroscopic studies were carried on Agilent Technologies Cary 100 UV-vis. ICP-MS measurements were done on Agilent Technologies 7900.

Gram-negative bacterial strain Escherichia coli (E. coli, ATCC25922) and Gram-positive bacterial strain Staphylococcus aureus (ATCC25923) were adopted in this study. The bacteria were initially streaked from -80°C glycerol stocks on lysogeny broth (LB). After growth on LB agar plates, the cells were cultured from a fresh single colony in LB. All experiments were conducted at 37 °C. Heterotrophic plate count measurement (HPC) was used in this study to quantify the bacteria. All glassware used in this study were sterilized before test.

2. Syntheses of PVA-TP-COOH and PVA-TP-CA

As illustrated in Scheme S1, 1.0 g of PVA-COOH (2.27 mmol -COOH), 0.28 g of 2-([2,2':6',2''-terpyridin]-4'-yloxy)ethan-1-amine (TP, 0.4 eqv. to carboxyl group), 0.17 g 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 0.4 eqv. to carboxyl groups) and 4-(dimethylamino)pyridine (DMAP, 0.4 eqv. to carboxyl group) were dissolved in a mixture of
DMSO. Then mixture solution was gently stirred overnight at room temperature and dialyzed in MeOH for 3 days. The ¹H NMR spectrum of PVA-TP-COOH is shown in Figure S1. The grafting density of TP groups to carboxyl groups was calculated as 4% based on the ¹H-NMR result.

![Figure S1. ¹H NMR spectrum (400 MHz, DMSO-d₆, 293K) of PVA-TP-COOH.](image)

![Scheme S2. Synthesis of PVA-TP-CA.](image)

As illustrated in Scheme S2, 0.3 g of PVA-TP-COOH (0.0026 mmol -COOH) and 0.78 g of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 1.5 eqv. to carboxyl groups) were dissolved in a mixture of MeOH and pH 4.8 2-(N-morpholino) ethanesulfonic acid (MES, 0.1 M) buffer (60 mL, 1v/1v). Then 0.78 g of dopamine hydrochloride (1.5 eqv. to amino groups) were added into the mixture and gently stirred overnight at room temperature. After removal of the solvent in a vacuum, the final residue was dialyzed in MeOH for 3 days. For higher stability and better storage, a small amount of 37% HCl was added before drying the polymer PVA-TP-CA. The ¹H NMR spectrum of PVA-TP-CA is shown in Figure S2.¹ The grafting density of catechol groups to carboxyl groups was calculated as 6% based on the ¹H-NMR result.
3. Synthesis of metal ions-incorporated PVA-TP-CA coating

Activating the silicon wafers:
The silicon wafers with the size of 1 × 1 cm² were first activated by H₂SO₄ and H₂O₂ with the volume ratio of 1:1. Then silicon wafers were rinsed with distilled water and MeOH three times and finally nitrogen-dried before coating.

PVA-TP-CA coating:
The freshly cleaned silicon wafers were immersed in a dilute aqueous solution of polymer PVA-TP-CA (3 mg/ml), then adjusted the pH to alkaline conditions by addition of 3-(N-morpholino)-propanesulfonic acid (MOPs) buffer (pH 8.5) for 2, 4, 8, or 12 h to prepare the PVA-TP-CA surface coatings. The catechol groups on the polymer underwent oxidative polymerization and generated aggregates that were resistant to common organic solvents, consequently resulted in the formation of an adherent polymer film on silicon wafer surface. The coated silicon wafers were thoroughly rinsed with water and MeOH, and dried by an Argon stream.

Metal ions-incorporated PVA-TP-CA coating:
The formed PVA-TP-CA surface coating was further immersed in the CoCl₂ aqueous solution (2 mg/ml) for 1 h to obtain the Co^{II}-incorporated PVA-TP-CA coating. Fe^{II}-incorporated PVA-TP-CA coating and Zn^{II}-incorporated PVA-TP-CA coating are prepared with the same procedure.

4. Scanning electron microscopy (SEM)
The surface morphology of the coating was investigated with a field emission scanning electron microscope (FE-SEM, Hitachi SU8030, Japan) at an accelerating voltage of 10 kV, a current of 10 μA and a working distance (WD) of around 8.3. The samples were dried under high vacuum and coated with a 8-10 nm gold layer by using a sputter coater (Emscope SC 500, Quorum Technologies, UK) for 20 s at 30 mA, 10⁻¹ Torr (1.3 mbar) in a argon atmosphere.
5. X-ray Photoelectron Spectroscopy (XPS)

XPS were recorded on a Kratos Axis Ultra DLD spectrometer equipped with a monochromated Al Kα X-ray source using an analyzer pass energy of 80 eV for survey spectra and 20 eV for the core level spectra. The electron emission angle was 60° and the source-to-analyzer angle was 60°. The binding energy scale of the instrument was calibrated following a Kratos analytical procedure that uses ISO 15472 binding energy data. Spectra were recorded by setting the instrument to the hybrid lens mode and the slot mode providing approximately a 300 x 700 μm² analysis area using charge neutralization. All XPS spectra were processed with the UNIFIT program (version 2017). A Gaussian/Lorentzian sum function peak shape model GL (30) was used in combination with a Shirley background. If not otherwise denoted, the L-G mixing for component peaks in all spectra were constrained to be identical.

6. Water contact angle measurement

The contact angle (θ) measurement was performed using a Dataphysics contact angle system OCA (Data Physics Instruments, Germany) together with the software package SCA202 version 3.12.11. The sessile drop method was used in this work. A liquid drop of the volume of 3 μL of Milli-Q water was placed on the substrate and allowed to equilibrate for 15 s at room temperature. At least eight measurements were performed to get a reliable value.

7. Antibacterial activity

*E. coli* and *S. aureus* bacterial suspension used in the antibacterial test were 10⁵ CFU/mL in phosphate buffered saline (PBS), respectively (CFU represents for colony forming units). First, the samples were placed into a standard 24-well culture plate. And then 500 μL of corresponding bacterial suspension was added into each well. After that, the cultures and the samples were incubated in an incubator (B6060, Heraeus, Germany) at 37 °C for 24 h. Then, 100 μL of planktonic bacterial suspensions were serially diluted and added onto the nutrition agar plates, respectively. The bacterial colonies were recorded after incubation at 37 °C for 24 h. Each experiment was repeated three times.

8. Atomic Force Microscopy (AFM)

The AFM results were recorded by a NanoWizard 2 scanning probe microscopy (SPM) system (Bruker, USA) in the water under ambient conditions. The commercially available AFM cantilever tips (MLCT-D, Bruker) with a force constant of ~ 0.03 N/m were used. The Contact
Force Spectroscopy Mode was used to get full force curves. The extend velocity was set to 2 μm/s.

9. In vitro Co\textsuperscript{II} ions release experiments

The purpose of this test was to measure the amount of Co\textsuperscript{II} ions released from the surface of PVA-TP-CA/Co coating. The samples were immersed in the volume of 500 μL of PBS and buffered BSA solution (3.5%, w/v), respectively. To evaluate the accumulative release of Co\textsuperscript{II} ions, the solution (100 μL) was extracted in different time, ranging from 2 h, 4 h, 8 h, 12 h, 24 h, 2 d, 3 d, 5 d, 7 d, 10 d, 14 d, 20 d, and up to 30 d, and fresh PBS and buffered BSA solution (100 μL) was instead added into the sample chamber for continuing incubation, respectively. The corresponding extracts were diluted in 1% HNO\textsubscript{3} containing 1 μg/L rhodium ICP-MS standard (Rh) as internal standard before testing. Co (m/z = 59) and Rh (m/z = 103) were quantified by external calibration using the on-mass mode and He (3 mL/min) as collision gas to avoid interferences. The amounts of the Co\textsuperscript{II} ions released from the PVA-TP-CA/Co coating were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies 7900).

10. Cell culture

MSCs were purchased from EMD Millipore (Darmstadt, Germany) and cultured in DMEM (Gibco 11965092) supplemented with 10% bovine growth serum (Gibco 16030074) and 1% penicillin/streptomycin (Gibco 15140122) at 37 °C with 5% CO\textsubscript{2}. The osteogenic differentiation medium (C-28013) was obtained from Promo Cell (Heidelberg, Germany). The cells were passaged twice a week according to the standard protocols. The fourth to sixth passages of MSCs were used in this study.

11. Immunocytochemistry

After culturing on bare silicon wafer, PVA-TP-CA surface coating and PVA-TP-CA/Co surface coating in DMEM medium for set time, the cells were fixed with 4% formaldehyde for 30 min at room temperature, permeabilized with 0.25% Triton X-100 in PBS for 10 min. The non-specific binding epitopes were blocked with 1% BSA in PBST (PBS with 0.1% Triton X-100) for 45 min at room temperature. Next, the cells were incubated with primary antibodies overnight at 4 °C. The primary antibodies used in this work are: mouse monoclonal anti-Paxillin (BD Transduction LaboratoriesTM 612405, 1:100 dilution), rabbit monoclonal anti-YAP (cell signaling 4912S, 1:200 dilution. After the incubation, cells were washed with PBS two times
and then incubated with the appropriate secondary antibodies (Invitrogen, goat anti-mouse IgG Alexa Fluor 488 A-11029 or goat anti-rabbit Alexa Fluor 568 A-11011, 1:500 dilution) for 1 h at room temperature. Finally, the cells were stained with DAPI (Sigma D9542, 1:1000 dilution) and Phalloidin-iFluor 647 (Abcam ab176759, 1:1000 dilution) and imaged by Zeiss Axio Observer Z1 phalloidin microscope (Zeiss, Germany) or a confocal microscope (SP8, Leica).

12. hMSCs differentiation and alkaline phosphatase (ALP) staining and quantification
The MSCs were seeded on bare silicon wafer, PVA-TP-CA surface coating and PVA-TP-CA/Co surface coating in basal growth medium with density of 5000 cell/cm² in 24 well plates for 24 h. Afterwards the medium was replaced by standard osteogenic differentiation medium for one week. The culture medium was replaced every 3 days. Alkaline phosphatase (ALP) activity was measured after incubation for 14 days using an ALP Activity Fluorometric Assay Kit (BioVision). Briefly, at desired time points, the samples were collected and washed with DPBS and ground in assay buffer. After centrifugation at 13,000g for 3 minutes at 4 °C, the supernatant (110 μL) was co-incubated with 20 μL of 4-methylumbelliferyl phosphate disodium salt (MUP, 0.5 mM) for 30 min at room temperature in dark, and then, 20 μL of the stop solution was added. The plate was gently shaken and measured with a microplate reader at an excitation wavelength of 360 nm and an emission wavelength of 460 nm. ALP activity was normalized to the total protein content of each well to determine the ALP index. The ALP staining was performed according to the manufacturer’s protocol (ALP Live Stain Kit, Thermo Fisher Scientific). Then observed via a confocal microscope (SP8, Leica).

13. Cell viability assays
The cytotoxicities of PVA-TP-CA surface coating and PVA-TP-CA/Co surface coating were evaluated by MTT assay with hMSCs. For the MTT assay, the cells were seeded onto the surfaces of the coatings placed in 24-well plates at a concentration of 2,000 cells per well. After 24 h and 72 h incubation respectively, the culture medium was replaced by 300 μL of pre-prepared MTT solution. After 4 h of incubation, the culture medium as well as the unreacted MTT agent was carefully removed. In each well, 300 μL of dimethyl sulfoxide was added to dissolve the blue formazan crystals. The optical density was measured by a microplate reader at 570 nm.

14. Statistical analysis
Data are represented as mean ± standard deviation (S.D). Group differences were conducted by one-way ANOVA with Tukey’s post-hoc test. P-values < 0.05 were considered as statistically significant (*p < 0.05, **p < 0.01, ***p < 0.001, ****p < 0.0001). All statistical analyses were performed with GraphPad Prism 8.

**Figure S3.** SEM images and water contact angles of different surface coatings.

**Figure S4.** UV/vis spectra of (a) CA in the absence and presence of excess CoCl₂ in DMSO/H₂O (v/v, 1:1), (b) addition of excess CoCl₂ into TP, PVA-TP-CA, and CA solution in DMSO/H₂O (v/v, 1:1), respectively, (c) TP without and with excess CoCl₂ in DMSO/H₂O (v/v, 1:1), (d) CA in the absence and presence of excess CoCl₂ in DMSO/MOPS buffer(v/v, 1:1), (e) addition of excess CoCl₂ into TP, PVA-TP-CA, and CA solution in DMSO/MOPS buffer(v/v, 1:1), respectively, and (f) TP without and with excess CoCl₂ in DMSO/MOPS buffer (v/v, 1:1).

The coordination interactions between Co^{II} ions and 2-((2,2':6',2”-terpyridin]-4'-yloxy)ethan-1-amine (TP), dopamine hydrochloride (CA), and PVA-TP-CA polymers were studied by UV-vis spectroscopy, respectively. Considering the limitation of UV-vis absorption, lower concentrations with the same ratios (compared to the practical protocol of coating preparation)
of PVA-TP-CA (0.0625 mg/mL), CoCl$_2$ (2.5 × 10$^{-3}$ mM) and corresponding TP (1 × 10$^{-5}$ mM) and CA (1.5 × 10$^{-5}$ mM) were employed. The whole experiments were performed in DMSO/H$_2$O (v/v, 1:1) mixture, due to the different solubility of PVA-TP-CA, CA. The absorption of CoCl$_2$ in DMSO/H$_2$O solution was subtracted.

The UV-vis spectra of CA showed no difference in DMSO/H$_2$O solution before and after the addition of excess Co$^{II}$ ions (Figure S4a). While adding excess Co$^{II}$ ions to TP solution exhibited a new peak at 308 nm, indicating the formation of a metal–ligand complex between TP and Co$^{II}$ ions in DMSO/H$_2$O solution (Figure S4c). Similarly, a new peak emerged at 304 nm after injecting the Co$^{II}$ ions into the PVA-TP-CA solution (Figure S4b), indicating the coordination with the TP units on polymer PVA-TP-CA in DMSO/H$_2$O media.

To further evaluate the possible coordination between Co$^{II}$ ions and the residual catechol groups on the crosslinked coatings, we employed the Co$^{II}$ ions to interact with CA and PVA-TP-CA in MOPS buffer (pH 8.5)/DMSO mixture (v/v, 1:1) and monitored the reaction by the UV-vis spectroscopy, as alkaline solution can trigger the deprotonation and oxidation of catechol, and the formation of metal–catecholate complexes.$^{55}$ The absorption spectrum of Co$^{II}$ ions in MOPs buffer was subtracted.

Compared to the UV-vis spectrum of Co$^{II}$ ions with CA in DMSO/H$_2$O (v/v, 1:1), a new broad peak emerged from 450 to 650 nm ($\lambda_{\text{max}} = 607$ nm) in the alkaline condition (Figure S4d). It might be attributed to the formation of a complex composed of Co$^{II}$, semiquinone and aminochrome, which were generated from the oxidation of dopamine in the case of Co$^{II}$ ions in alkaline solution.$^{55b}$ While the absorption spectra of TP-Co$^{II}$ complex in DMSO/H$_2$O (v/v, 1:1) and DMSO/MOPs buffer (v/v, 1:1) were almost the same. Only a slight red shift from 453 nm (neutral condition) to 463 nm (alkaline condition) can be observed (Figure S4f). For the PVA-TP-CA and Co$^{II}$ ions in DMSO/MOPs buffer (v/v, 1:1), except for the remarkable peak at 308 nm belonged to the complexation between Co$^{II}$ ions and TP units on the polymer backbone, a new broad peak with low absorption intensity around 556 nm was observed in the absorption of (PVA-TP-CA)-Co$^{II}$ complex compared to that in DMSO/H$_2$O (v/v, 1:1) (Figure S4e). Combining the UV-vis spectra of TP-Co$^{II}$ complex and CA-Co$^{II}$ complex, this new appeared peak around 556 nm should be an integrated outcome of the interaction of Co$^{II}$ ions with TP and residual oxidative CA in alkaline solution.

In summary, Co$^{II}$ ions can interact with TP units on polymer PVA-TP-CA backbone despite of the environmental pH, while it can only complex with CA moieties in the alkaline solution. Therefore, due to the chelation between metal ions and ligands (TP and oxidative CA) on the polymer backbone, Co$^{II}$ ions were stabilized in the surface coating networks.
Figure S5. Bacterial number on the PVA-TP-CA/Co and PVA-TP-CA surface coatings on TC4 titanium alloy, and bare TC4 titanium alloy against E. coli and S. aureus suspension. Data are presented as the mean ± SD, n = 3. Statistically significant differences at the same period are indicated by **p < 0.01 compared with Blank Control.

Figure S6. Antibacterial abilities of CoII ions with different concentrations against E. coli suspension.

The antibacterial result of CoII ions with different concentrations ranging from 1 to 15 ppb showed no antibacterial ability towards E. coli, indicating the tiny released amount of CoII ions with 13.1 ppb from PVA-TP-CA/Co coating that immersed in buffered BSA solution for 30 days was nontoxic towards bacteria.
Figure S7. Three rounds of continuous antibacterial tests against *S.aureus*.

Figure S8. The cell aspect ratios on different surfaces.

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