Covalent Modification of UiO-66-NH_2 by Copper-Schiff Base to Construct Multifunctional Coating on Medical Magnesium Metal Surface

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Abstract Medical magnesium metal is widely used in bio-implantable materials due to its excellent Young's modulus and unique degradable properties [1]. However, the highly reactive nature of magnesium makes it highly susceptible to uncontrollable corrosion, as well as functional degradation [2]. Metal-organic frameworks (MOFs) have gained extensive attention in recent years due to their high surface area, multifunctional groups, and various chemical activities [3]. This paper focuses on constructing an inner coating of NH_4TiOF_3 for corrosion protection and an outer coating of MOF with catalytic functionality on magnesium metal surfaces (Fig.1). The composite coating provides both corrosion protection and multifunctionality. The compact structure of MOF coating on pure magnesium shows strong bonding to the substrate and long-term corrosion protection during in vitro saline immersion tests (Fig.2 a-c). Additionally, the covalent grafting of Schiff base chelated metal ions with the amino groups of UiO-66-NH_2 MOF enables the creation of a biomultifunctional catalytic platform. Cu, as a catalytic active site, effectively catalyzes the decomposition of endogenous GSNO to produce NO at a rate of 17 x 10^{-8} mol/cm²·min (Fig.2 d). Moreover, it exhibits more than 60% catalytic decomposition of H_2O_2 initially and inhibits hydroxyl radicals and superoxide anions by over 60% (Fig.2 e-g). This catalytic efficacy is maintained at 40%-30% after 14 days of immersion. The composite coating also demonstrates excellent biocompatibility and hemocompatibility, with MC3T3-E1 osteoblast viability consistently above 99% (Fig.2 h). Its protein desorption capacity is the highest for both BSA-FITC and FBG-FITC proteins. Finally, due to the presence of Cu^{2+} and a localized alkaline microenvironment, the coating exhibits sustained

antibacterial performance against E. coli and S.aureus (Fig.2 i), with an antibacterial rate exceeding 99% after 14 days of immersion.

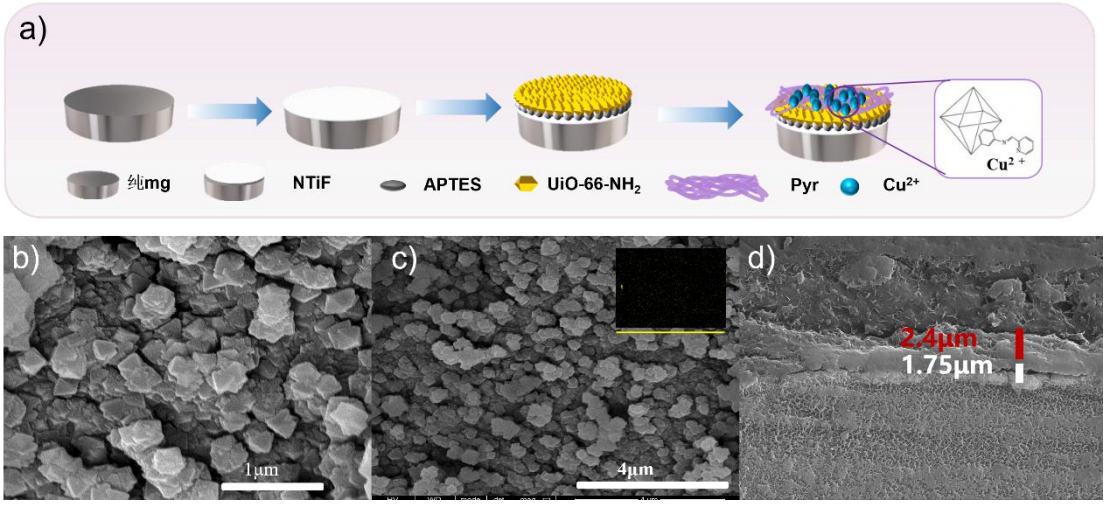

Fig.1. (a) Schematic diagram of composite coating prepared on magnesium-based surface. (b) SEM topography of the surface of UiO-66-Pyr specimen. (c) and (d) SEM topography of the surface and cross-section of the UiO-Pyr-Cu specimen.

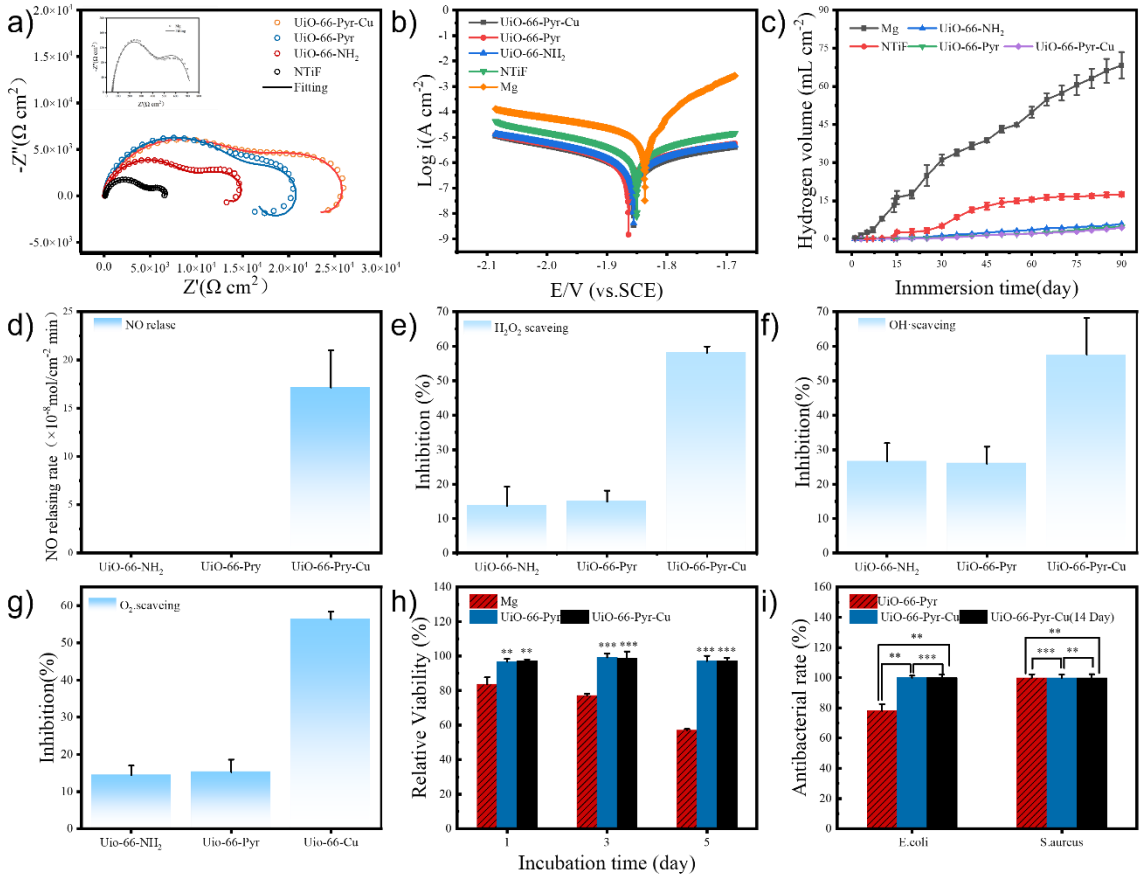

Fig.2. (a) EIS plots, (b) Tafel curves and (c) hydrogen evolution curves of different specimens after treatment. Different specimens initially (d) catalyzed generation of NO, (e) catalyzed decomposition of H_2O_2, and (f-g) catalyzed inhibition of ROS.(h) Relative cell survival of MC3T3-E1 cells cultured on different samples for 1, 3, and 5 days. (f) Antimicrobial rates of E. coli and S.aureus on different sample surfaces.

Keywords Metal-organic frameworks; Corrosion protection; Schiff bases; Biocatalysis; Biocompatibility; Antimicrobials.

Reference

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