One-step fluorine-free preparation of superhydrophobic coatings with antimicrobial and consolidation effects for the conservation of stone artworks

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In the outdoor environments, stone artworks suffer from severe degradation due to chemical, physical and biological phenomena triggered by acid rain, atmospheric pollutants/microbial spore depositions, etc. Liquid/gaseous water and soluble salts are the essential causes of stone weathering, and there is an urgent need to protect the surface layer of stone artworks against weathering. Recently, superhydrophobic materials with excellent hydrophobicity and self-cleaning properties show great potential as protective coatings, yet the poor consolidation effect and mechanical durability, insufficient antimicrobial property, as well as potential pollution/health risks upon fabrication impede their application. In this study, the coating sols were prepared via a one-pot fluorine-free method, by tuning the molar ratios between trimethoxyoctylsilane (TMOS), ZnO tetrapods (T-ZnO) and SiO_2 nanoparticles. To apply, superhydrophobic surfaces were obtained on substrates effortlessly by brushing/spraying and subsequent gelation of the sols. Exploiting the photocatalytic property and intrinsic bioactivity of T-ZnO, as-prepared coatings showed good biocidal effect. With a very low amount applied (10 g/m^2), the coating prepared with the ratio TMOS/SiO_2/T-ZnO=3/1/1 demonstrated the highest hydrophobicity (166°), as well as the best antimicrobial effects against both Gram-positive/negative bacteria (i.e., 82% and 78% respectively, with the concentration 2.0 mg/mL). Besides, the as-prepared coatings also exhibited high resistance to chemical erosion and mechanical abrasion (withstand 100-cycle tests), owing to the isotropic high mechanical/chemical strength of T-ZnO in the 3D. Moreover, by slightly increasing the coating amount to 30 g/m^2, the surface (0-10 mm) mechanical strength of the substrate improved (~20%), as evidenced by micro-drilling resistance tests. The mechanical strength originated from the polycondensation of TMOS in the presence of T-ZnO, in which T-ZnO acted as the skeleton fillers inside the silica gel networks to further enhance its strength in the three

dimensions. With the facile synthesis and desirable multi-functionalities, as-prepared coatings are promising for the sustained maintenance of outdoor built-heritage and stone artworks.