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Biomimetically synthesized luminescent Tb^{3+}-doped fluorapatite/agar nanocomposite for detecting UO_2^{2+}, Cu^{2+}, and Cr^{3+} ions†

Hongjuan Liu,[ab] Xianli Wang,[a] Thulitha Abeywickrama,[a] Forough Jahanbazi,[a] Zefu Min,[b] ZhengRong Lee,[c] Jeff Terry [cd] and Yuanbing Mao *[a]

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Radionuclides and heavy metal ions have become the main harmful pollutants in the environment. Developing sensitive and rapid methods to detect them from natural water or wastewater is important to reduce their exposure risks. In this study, a novel luminescent Tb^{3+}-doped fluorapatite/agar nanocomposite (Tb-FAP/agar) has been synthesized *via* a facile and green synthetic route through an environmentally friendly biomineralization process using agar as a template. This nanocomposite is the first luminescent fluorapatite for detecting UO_2^{2+}, Cu^{2+}, and Cr^{3+} ions in water with high selectivity and sensitivity based on luminescence turn-off effects. The detection limits of the Tb-FAP/agar for UO_2^{2+} (7.95 nM), Cu^{2+} (3.94 nM), and Cr^{3+} (1.67 nM) are much lower than the permissible limits in drinking water defined by the United States Environmental Protection Agency (USEPA). Furthermore, the luminescence detection mechanisms for UO_2^{2+}, Cu^{2+}, and Cr^{3+} ions were speculated. Our study provides insight into developing biodegradable rare earth doped fluorapatite probes for the detection of both radioactive and nonradioactive ions.

Environmental significance

Radionuclides and heavy metal ions have become the main harmful pollutants in the environment. Developing sensitive and rapid methods to detect them from natural water or wastewater is important to reduce their exposure risks. Here we synthesized a luminescent Tb^{3+}-doped fluorapatite/agar nanocomposite *via* an environmentally friendly biomineralization process and demonstrated its detection for UO_2^{2+}, Cu^{2+}, and Cr^{3+} ions in water with high selectivity and sensitivity based on luminescence turn-off effects. Its detection limits for these three ions are much lower than the permissible limits in drinking water defined by the United States Environmental Protection Agency (USEPA). Our findings indicated that luminescent nanocomposites can be environmentally friendly designed and explored as potential luminescence sensors for environmental monitoring applications.

1. Introduction

Hydroxyapatite [$(Ca_{10}(PO_4)_6(OH)_2$, HAP] is the main inorganic ingredient of vertebrate hard tissues such as bones and teeth.[1,2] It is a biodegradable, eco-friendly material with excellent biocompatibility and bioactivity. Moreover, HAP is a good host lattice for doping of rare earth (RE) ions. This is because the ionic radii of RE ions are close to that of Ca^{2+}, enabling their easy substitution for Ca^{2+} in HAP. HAP materials doped with RE ions such as Tb^{3+} and Eu^{3+} have potential applications as luminescent probes due to their excellent luminescence characteristics.[3,4] The fluoride ion (F^-) is usually used for replacing the hydroxyl (–OH) group of HAP to form calcium fluorapatite [$Ca_{10}(PO_4)_6F_2$, FAP] to further improve the luminescence properties because of the absence of the OH^- group that has a possible quenching effect on the luminescence of RE ions.[1,5] Meanwhile, the F^- ion generates lower vibration energy and promotes efficient luminescence conversion.[6,7]

Synthesis methods of HAP mainly include chemical precipitation,[8] sol–gel,[9,10] combustion,[11] hydrothermal,[12] microemulsion,[13] and biomineralization processes.[14] Among these methods, the biomimetic synthesis method operating under mild environment conditions does not need poisonous reagents, avoiding relying on high temperature, high pressure, strong acids and alkalis and harsh reaction

[a] *Department of Chemistry, Illinois Institute of Technology, 3101 South Dearborn Street, Chicago, IL 60616, USA. E-mail: ymao17@iit.edu; Tel: +1 312 567 3815*
[b] *School of Nuclear Science and Technology, University of South China, Hengyang, 421001, China*
[c] *Department of Physics, Illinois Institute of Technology, 3101 South Dearborn Street, Chicago, IL 60616, USA*
[d] *Department of Mechanical Materials, and Aerospace Engineering, Illinois Institute of Technology, 3101 South Dearborn Street, Chicago, IL 60616, USA*

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