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Turn-Off Fluorescence Detector for Cu^{2+} Ions; $GdVO_4$:Eu Nanoparticles

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Extended Abstract

Europium-doped gadolinium orthovanadate ($GdVO_4$:Eu) nanoparticles (NPs), which provide narrow and photobleaching resistant emissions, are currently successfully prepared and are attracting considerable attention for biomedical applications, such as multifunctional bio-probes capable of fluorescent probing as well as magnetic resonance imaging (MRI).[1] However, while extensive investigations for fluorescence imaging, magnetic relaxivity, and cytotoxicity revealed the excellent biocompatibility of $GdVO_4$:Eu NPs, [2] not much attention has been paid to elucidate the effect of transition metal ions that exist in the human body on the fluorescence probe function of $GdVO_4$:Eu NPs. For most biomedical applications of NPs, understanding the possible effects induced by adsorption of biologically important metal ions is an interesting issue because the adsorbed metal ions can affect the function of NPs to limit their sensitivity, performance, stability, and resolution in applications.

In this work, $GdVO_4$:Eu NPs were prepared using layered gadolinium hydroxychloride ($Gd_2(OH)_5Cl{\cdot}nH_2O$) as a precursor to react with *meta*-vanadate (VO_3^-) in aqueous solutions at room temperature. The large quantities of hydroxyl groups remaining on the surface make $GdVO_4$:Eu particles prepared by this route homogeneously dispersible in water without any further surface modification. Despite surface O–H oscillators, the emission from $GdVO_4$:Eu NPs prepared in the present work was sufficiently strong and easily monitored. As the adsorption and true toxic effects of metals arise mainly from metal ions, rather than elemental metals or their stable organic/inorganic complexes, [3] the adsorption of metal ions on the $GdVO_4$:Eu particles was performed in aqueous $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $ZnCl_2$, $CdCl_2$, $PbCl_2$, and $AlCl_3$ solutions at room temperature. Interestingly, plots of the excitation and emission intensities of the $GdVO_4$:Eu NPs showed quite different quenching behaviors depending on the type of adsorbed metal ion. Compared to essentially no influence of the Mg^{2+}, Ca^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Al^{3+} ion adsorptions, significant quenching of the $GdVO_4$:Eu emission was achieved within 3 min with the adsorption of Cu^{2+}. We attributed this difference to the absorption of the emitted light by adsorbed Cu^{2+} ions through the so-called 'inner filter effect'. Because such a filter effect can effectively occur only if the absorption band of the metal ion is complementarily overlapped with the emission bands of $GdVO_4$:Eu, highly selective and sensitive fluorescence quenching could be achieved by the Cu^{2+} ion adsorption. As a consequence, even if we consider that many Cu^{2+} ions may exist in the form of stable organic/inorganic complexes in the human body, the possibility of this filter effect on the fluorescence of $GdVO_4$:Eu nanoprobes cannot be ignored. Inversely, the high selectivity and sensitivity may make $GdVO_4$:Eu NPs a "turn-off" fluorescent sensing material to monitor and maintain a toxic Cu^{2+} concentration in environmental water.

References

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