Enhanced tuneable emission of environment-friendly Cu, Mn dopants modulated $ZnInSe_2$/ZnSe core/shell QDs for ultra-stable fluorescent anti-counterfeiting

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Doping in semiconductor quantum dots (QDs) with an optically active elements have become crucial to realize intriguing properties. Herein, we synergistically modulated the optical properties of eco-friendly $ZnInSe_2$/ZnSe core/shell QDs by incorporating Cu- and Mn- doping into their core and shell to investigate their potential implementation in anti-counterfeiting and information encryption. The engineered "Cu:$ZnInSe_2$/Mn:ZnSe" core/shell QDs exhibit an intense bright orange photoluminescence (PL) emission at λ = 606 nm, having a higher colour purity than the one of undoped and single-doped core/shell QDs. When compared to Cu:$ZnInSe_2$/ZnSe core/shell QDs, Cu:$ZnInSe_2$/Mn:ZnSe core/shell QDs exhibited an extended average PL lifetime of 201 ns is measured, which makes its relevant for complex encryption and anti-counterfeiting. Integration of Cu:$ZnInSe_2$/Mn:ZnSe core/shell QDs into poly(methyl methacrylate) (PMMA) can serve as versatile smart concealed luminescent inks for both writing and printing patterns. The characteristics of the printed patterns using Cu:$ZnInSe_2$/Mn:ZnSe core/shell QDs are found to sustained after direct water-soaking for 10 weeks. A remarkable 70% retention of its PL emission is reported when heated at 170 °C, featuring its excellent thermal stability. The photo-emission mechanism of Cu:$ZnInSe_2$/Mn:ZnSe lies on the predominant contribution of the Cu state emission, , as supported by the PL and time decay measurements. The isolation of Cu and Mn dopants inside the core and shell regions of the host $ZnInSe_2$/ZnSe core/shell QDs not only reduces the energy transfer between the activators ($Cu^{+} \rightarrow Mn^{2+}$) but significantly improve the luminescence intensity and durability. This work provides an efficient approach to simultaneously enhance both the emission and the stability of eco-friendly QDs using dopants for fluorescence anti-counterfeiting applications.

Keywords: Dopants; Copper; Quantum dots; Core/shell; Manganese; Anti-counterfeiting