Eu (III) doped downconverting nanophosphors (GdVO₄:Eu³⁺) for selective and sensitive detection of arsenic (III) in water

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Materials

Analytical-grade chemicals and reagents were utilised throughout without further purification. $Gd(NO_3)_3.6H_2O$, $Eu(NO_3)_3.6H_2O$, Arsenic trioxide (As_2O_3) and Ammonium metavanadate (NH_4VO_3) were acquired from Sigma-Aldrich. $Na_3C_6H_5O_7$ (tri-sodium citrate), NaOH (sodium hydroxide pallets) and ethanol (C_2H_5OH) was purchased from Spectrochem Pvt. Ltd. Triple-distilled water was utilized as a solvent throughout the synthesis process. Aqueous solutions of Na⁺, Ag⁺, Ca²⁺, Cd²⁺, Co²⁺, Fe³⁺, Cs⁺, Fe²⁺, Mg²⁺, Hg²⁺, In³⁺, K⁺, Mn²⁺, Ni²⁺, and Pb²⁺, Sn²⁺ and Zn²⁺ were made from the corresponding halide salts.

Characterization

The nanophosphors were subjected to morphological characterization by field emission scanning electron microscopy (FESEM), MERLIN Zeiss-Germany. For TEM analysis, the suspension of nanophosphors was deposited on a copper TEM grid with a carbon film (TED Pella). To confirm the exact shape and size of the nanophosphors, transmission electron microscopy (TEM) was carried out using a TECNAI G2 -30 U TWIN (FEI, Eindhoven, Netherlands) instrument operated with an accelerated voltage of 300 kV. The average hydrodynamic diameter of the nanophosphors was measured by dynamic light scattering (DLS), using a NANO-ZS series Malvern Zetasizer instrument. Powder X-ray diffraction measurement was done to analyze the phase composition and crystalline nature of nanophosphors using a Bruker D8 Discover X-ray spectrometer, which utilizes Cu Ka radiation (λ = 1.54060 Å) over the 2 θ range (of 10 to 70) at the scanning rate of 2.58/min. FT-IR spectra were taken from 4000 to 400 cm⁻¹, where the dried and powdered nanophosphors were mixed with KBr and the mixture was pressed into a pellet for analysis using a PerkinElmer RX1 spectrometer. The absorbance and fluorescence spectra were observed using a Shimadzu UV-1601 spectrophotometer (Shimadzu, Kyoto, Japan) and a Cary Eclipse fluorescence spectrometer (Varian, Palo Alto, CA), respectively.



Figure S1: (A) TEM image and (B) Histogram distribution plot for synthesised DCNPs.



Figure S2: Relationship between ($\beta \cos \theta$) and (sin θ) of DCNP.



Figure S3: TGA spectrum of as-synthesised DCNPs (GdVO₄:Eu³⁺).



Figure S4: Photoluminescence emission spectra of GdVO₄ (black curve) and Eu^{3+} -doped GdVO₄: Eu^{3+} (red curve) under excitation at 273 nm.



Figure S5: (A) Emission spectra of synthesised DCNPs at different doping concentration of Eu (B) Time-dependent emission spectra of DCNP (λ_{Ex} = 273 nm).



Figure S6: Schematic diagram of the interaction of As³⁺ with the DCNPs that lead to the emission quenching of the latter.



Figure S7: Emission intensity of DCNP (at 619 nm) upon addition of As³⁺ ions (30 μ M) as a function of time.



Figure S8: (A) photoluminescence emission spectra of DCNP in buffer solution at various As³⁺ ions concentrations under UV-light excitation ($\lambda_{Ex} = 273$ nm). Inset: emission Intensity (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) magnitude at 619 nm at various concentrations. (B) Linear fitting curve of I_o/I for the emission intensity of DCNP with respect to the concentration of As³⁺ over the range from 0 - 60 μ M in buffer.



Figure S9: (A) Change in absorbance of DCNP upon addition of As^{3+} ions. (B) Variation in relative absorbance with As^{3+} ions in the concentration range of 0 - 50 μ M.