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In Situ Functionalized Fluorescent WS_2-QDs as Sensitive and Selective Probe for Fe^{3+} and a Detailed Study of Its Fluorescence Quenching

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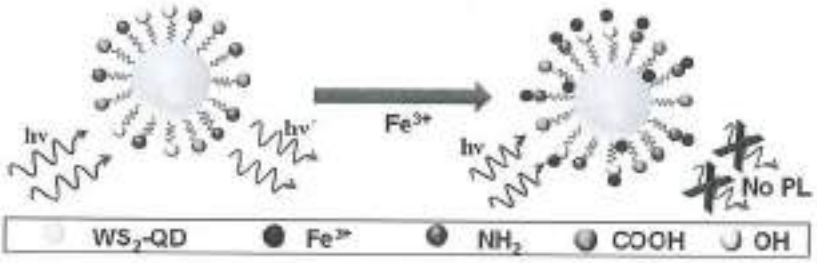
Supporting Information



ABSTRACT: Most of the reports suggest that liquid exfoliated WS_2-QDs are unstable; therefore the need of present day is to develop a novel synthesis route for producing long-term stable WS_2-QDs. Herein, we report a bottom-up single-step hydrothermal growth of in situ functionalized blue fluorescent WS_2-QDs with stable fluorescence in aqueous media without subsequent treatments. Presence of various functional groups over the surface of f-WS_2-QDs provides high solubility and stability to f-WS_2-QDs in aqueous media preserving its fluorescence. Further, photoluminescence property of f-WS_2-QDs has been employed to devise an optical sensor with a high sensitivity ($K_D \sim 10^6\ M^{-1}$) and selectivity for ferric (Fe^{3+}) ions. Under the optimal condition, response of the sensor is found to be linear in the range of 0−55 μM with a limit of detection (LOD) of 1.32 μM, which is within the maximum permissible level of Fe^{3+} (~5.4 μM) in human drinking water by the USEPA. Further, we have also carried out a detailed evaluation on fluorescence quenching kinetics of f-WS_2-QDs. Nonlinear behavior of S−V plot and TRPL measurements suggest that quenching is a mixed phenomenon of dynamic as well as static processes. Finally we have proposed a mechanism for fluorescence quenching of f-WS_2-QDs in the presence of Fe^{3+}.

KEYWORDS: *WS_2, quantum dots, hydrothermal synthesis, quantum yield, TRPL, fluorescence quenching*

INTRODUCTION

In the post-graphene era, a great sensation has been observed in the current research on layered transition metal dichalcogenides (LTMDs) of few-to-monolayer nanocrystals (NCs) or quantum dots (QDs) of MoS_2, WS_2, $MoSe_2$ etc., which have been conceived as best substitutes of graphene and carbon QDs.[1−4] In this LTMDs series, 2D WS_2 has aroused even greater attention owing to its controllable band gaps as a function of layer numbers with remarkable optical and electronic properties.[5−7] WS_2 is a van der Waals layered material with hexagonal lattice structure arranged in triple layers (S−W−S); each layer has a thickness of 6 Å with strong in-plane covalent bonding and weak out-of-plane van der Waals interactions.[8] Further, by reducing the lateral size of 2D WS_2 sheet in 0D WS_2-QDs, one can acquire excellent electrical/optical behaviors from these NCs due to their strong quantum confinement and edge effects.[9] In addition to this, WS_2-QDs possess larger surface to volume ratio and much more active sites beyond monolayer 2D WS_2, which may be beneficial for sensing, catalysis, bioimaging, etc. To date,

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