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FULL PAPER

pH Dependent Optical Switching and Fluorescence Modulation of Molybdenum Sulfide Quantum Dots

*Himanshu Mishra, Sima Umrao, Jai Singh, Rajesh Kumar Srivastava, Rashid Ali, Arvind Misra, and Anchal Srivastava**

Investigations on fluorescent molecules with fluorescence switching behavior as function of pH, temperature, ion concentration, etc. is highly desirable in the field of sensor device fabrication. In this study, the authors report an easy and eco-friendly hydrothermal route for the synthesis of pH dependent fluorescent MoS_2 quantum dots (MoS_2-QDs). The average size of the synthesized QDs is found to be ≈7 nm which was confirmed with transmission electron microscopy and atomic force microscopy. These MoS_2-QDs show the pH dependent fluorescence switching behavior. Under pH = 1 the fluorescence intensity of the MoS_2-QDs is quenched while it shows ≈200 times enhancement under pH = 13. This florescence ON/OFF switching is mainly due to the surface adsorbed functional groups ($-NH_2$, SO_4^{2-}, OH^-, etc.) and is a combined effect viz. protonation–deprotonation process, acid etching, quantum confined Stark effect and particle agglomeration. A plausible mechanism for this pH dependent ON/OFF switching behavior is also discussed in this study. The band gap calculation under different pH environment is also in good agreement to the hypothesis.

1. Introduction

Semimetallic nature of graphene limits its applicability in the field of electronics and optoelectronics.[1] Recently, MoS_2 has been extensively studied as an alternative of graphene in the field of low dimensional electronics and optoelectronics.[2,3] Monolayer, 2D MoS_2 possess similar properties to graphene but with finite direct band gap (≈1.8 eV).[4] In MoS_2, one metal (Mo) layer is sandwiched between two sulfur layers forming an edge linked octahedral unit. The different layers of MoS_2 are bonded to each other with van der Waals forces which allowed them to be cleaved easily along their basal planes. The atoms of MoS_2 forms a close packed triangular crystal structure. Due to its 2D confinement of electron motion and absence of interlayer perturbation, monolayer MoS_2 offers new opportunities in various areas, such as sensors, single layer based transistors, integrated circuits, phototransistors, photovoltaic, etc.[3,5]

Following the research into 2D materials, 0D materials (quantum dots [QDs]) have also attracted great attention due to their several fascinating physical and optical properties. QDs are the nanostructure confined in all the three directions. The functionalities of QDs can be simply tailored by controlling the size, edge and compositions.[6] QDs shows better response over conventional dyes in terms of photo physical properties, size tunable brightness, resistance against photo bleaching, and simultaneous excitation colors.[7] In this contrast earlier florescence property of several QDs viz. CdSe, ZnS, PbS, GQDs, etc. have been extensively studied.[8,9] It is believed that MoS_2-QDs could be also used in very similar kind of applications to other QDs. However, MoS_2-QDs have not been thoroughly investigated. Earlier it was reported that monolayer MoS_2 shows ≈10^3 times enhancement in photoluminescence (PL) intensity than its bulk counterpart.[4] There are also several reports which show that 0D MoS_2 shows prominent fluorescence intensity.[10–12] Gopalakrishnan et al.[11] have used the ultrasonication followed by ultrasound probe sonication for the synthesis of heterodimensional MoS_2 and used it for hydrogen evolution reaction (HER). Li et al.[13] have synthesized MoS_2-QDs using electrochemically induced Fenton reaction with variable reaction time. Wang and Ni[12] have used hydrothermal synthesized fluorescent MoS_2-QDs for the detection of 2, 4, 6-trinitrophenol. Xu et al.[14] have used a combination of sonication and solvothermal to synthesize the MoS_2/WS_2 QDs with lateral size of ≈3 nm. They used the as synthesized monolayer MoS_2/WS_2 QDs for in vitro imaging and HER. Ha et al.[10] have synthesized the MoS_2-QDs using the Li^+ ion intercalation and studied its capability as a fluorescent tag in

H. Mishra, Dr. S. Umrao, Dr. A. Srivastava
Department of Physics
Institute of Science
Banaras Hindu University
Varanasi 221005, India
E-mail: anchalbhu@gmail.com
Dr. J. Singh
School of Mathematical and Physical Sciences (MPS)
Dr. Harisingh Gour University
Sagar 470003, India
Dr. R. K. Srivastava
Department of Physics
Indian Institute of Sciences
Banagalore 560012, India
R. Ali, Dr. A. Misra
Department of Chemistry
Institute of Science
Banaras Hindu University
Varanasi 221005, India

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