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Defect induced photoluminescence in MoS_2 quantum dots and effect of Eu^{3+}/Tb^{3+} co-doping towards efficient white light emission

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ABSTRACT

Intensive research has been carried out on optical properties of MoS_2 quantum dots for versatile applications in photo catalytic, sensing and optoelectronic devices. However, white light generation from MoS_2 quantum dots particularly using doping effect is relatively unexplored. Herein we report successful synthesis of Europium (Eu)/Terbium (Tb) co-doped MoS_2 quantum dots to achieve white light for potential applications in optoelectronic devices. The dopant ions are introduced into the host lattice to retain the emission colors to cover the entire range of visible light of solar spectrum. Perfect white light (CIE = 0.31, 0.33) with high intensity (quantum yield = 28.29%) is achieved in these rare earth elements co-doped quantum dot system. A new peak is observed in the NIR region which is attributed to the defects present in MoS_2 quantum dots. Temperature dependent study has been carried out to understand the origin of this new peak in the NIR region. It is seen that the 'S' defects in the QDs cause the appearance of this peak which shows a blue shift at higher temperature.

1. Introduction

In recent time, semiconducting quantum dots (QDs) viz. MoS_2 QDs have received wide attention because of their significant inherent characteristics like electronic, and photoluminescence properties. Due to excellent optical properties, large surface area, superior chemical durability, biocompatibility and lower cytotoxicity, MoS_2 QDs based systems have been extensively used as multi-photon bio-imaging labeling [1–3]. Optical properties of semiconductors are related to the band structure of the material. MoS_2 quantum dots can show fascinating optical properties due to their quantum confinement effect, and it makes them very suitable candidate for generating novel optoelectronic and sensing devices [4]. Now-a-days, an intense interest has been paid to the research on white-light emission from semiconductor nanostructures since it can replace the traditional light sources to reduce the energy costs. Currently, the method to achieve perfect white light is the combination of phosphors or nanocrystals having three primary colors (red, green and blue) using multilayer structures in LEDs; but through the simple mixing of these nanocrystals often leads to less intense white light due to uninvited energy transfer and this may lead to inferior white light efficiency [5]. One way to achieve white light with satisfactory Commission International d Eclairage (CIE) coordinates is the easy chemical synthesis of doped semiconductor nanocrystals. In this context, Mn^{2+}-doped CdS [6]and ZnS [7,8] NCs with white-light emission have been successfully prepared by the combination of the orange emission from the Mn^{2+} ions and the blue-green emission originating from the surface defect states present in the semiconductor lattice. A facile method was developed for the synthesis of the bright green-red-emitting Mn and Cu co-doped Zn–In–S QDs to generate bright natural white light with CIE color coordinate of (0.34, 0.36) [9]. There is another report on the synthesis and optical properties of pristine graphene oxide quantum dots (GOQDs) which can generate white light having CIE coordinates (x = 0.29, y = 0.34) [10]. Core-shell structures of quantum dots doped with different ions are another class of materials to achieve white light emission. There is a recent report on controllable synthesis and optical properties of ZnS:Mn^{2+}/ZnS/

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ZnS:Cu^{2+}/ZnS Core/Multishell Quantum Dots to get efficient white light emission with CIE coordinates of (0.32, 0.34) [11]. To the best of our knowledge, there is no such report available in literature where rare earth ion doped MoS_2 quantum dots have been used for perfect white light emission. Rare earth ions have excellent emission properties when they are incorporated into a suitable host lattice where the ions do not suffer from non-radiative emission due to the phonon structure of host lattice. On the other hand, defects induced photoluminescence in transition metal dichalcogenides (MoS_2, WS_2, and $MoSe_2$) have recently attracted much attention to the researchers due to the fact that tuning of the defect luminescence can be potential to enrich the optical properties of TMDs [12–14]. Anionic vacancy defects centers, were proposed to play the main role in originating the defect induced PL in TMDs. In case of monolayer MoS_2, photoluminescence from sulfur vacancies were reported by different researchers [14] at around 1.7 eV below the characteristic band gap emission of MoS_2. Moreover the defects related photoluminescence were also found to increase considerably by tuning the number of vacancy centers either by annealing thermally or by high energy irradiation. Though there are few research already been reported on the defect induced PL in TMD monolayer [14–16] but till date no research is reported on photoluminescence from defect states in TMDC quantum dots especially on MoS_2 quantum dots.

Here in this present work, we have reported successful synthesis of Europium (Eu)/Terbium (Tb) co-doped MoS_2 quantum dots from which white light emission has been achieved. The two dopant ions have been introduced into the host lattice in such a way that their emission colors can be retained to cover the entire range of visible light of solar spectrum. From our study, it can be shown that MoS_2 is a good host for incorporating rare earth ions with higher concentration. We have also shown that a perfect white light can be achieved by the system just by tuning the composition of rare earth ions and MoS_2 concentration. In addition, this is for the first time we report defect induced broad photoluminescence from MoS_2 quantum dots in the NIR region. The emission is proposed to be originated from single and double sulfur vacancy centers in MoS_2 lattice. The emission intensity is found to increase considerable with the decrease in temperature from 300 K to 77 K. Moreover an unusual blue shift of the defect induced emission peak is also observed with increase in temperature.

2. Experimental section

2.1. Materials

Molybdenum (IV) Sulfide powder, < 2 μm, 99% (Sigma-Aldrich); Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] (sigma-aldrich); L-Cysteine hydrochloride (Sigma-Aldrich); Buffer Solution (pH = 7.0) (Merck); Anhydrous Europium (III) Chloride ($EuCl_3$) (Sigma-Aldrich); Anhydrous Terbium (III) Chloride ($TbCl_3$) (Sigma-Aldrich); N,N-Dimethylformamide (DMF) (Merck); PUR-A-LYZER MEGA DIALYSIS KIT (Sigma-Aldrich); Mili-Q Water.

2.2. Synthesis of bare MoS_2 quantum dots (QDs)

100 mg of bulk molybdenum (IV) sulfide powder was dissolved in 60 mL of DMF: mili-Q water (4:1) solvent. It was sonicated for 48 h. After ultrasonication treatment, the decanted solution was refluxed at 145° C for 10 h under argon atmosphere. Finally, it was dialyzed using PUR-A-LYZER MEGA DIALYSIS KIT for 6 h and during the dialysis, the water was changed at an interval of 2 h [4].

2.3. Synthesis of amine (-NH_2) functionalized MoS_2 quantum dots (QDs)

Amine functionalized MoS_2 Quantum Dots (QDs) were synthesized using the following hydrothermal treatment. Then 50 mg of L-cysteine hydrochloride in 25 mL of mili-Q water was added to 10 mL aqueous solution of ammonium molybdate tetrahydrate. The resulting solution was stirred for 20 min. The pH of the overall mixture was strictly maintained to 7 using 5 mL buffer solution. Finally, it was transferred into 100 mL Teflon lined steel autoclave and treated hydrothermally for 24 h at 200° C. After hydrothermal treatment; the solution was dialyzed by PUR-A-LYZER MEGA DIALYSIS KIT against Mili-Q water for 24 h to remove unreacted chemicals as well excess capping agents [4,17].

2.4. Synthesis of europium (III) and terbium (III) co-doped amine (-NH_2) functionalized MoS_2 quantum dots (QDs)

5 mL of functionalized QDs solution in 10 mL mili-Q water was taken in 50 mL round bottom flask. 0.2 m(M) of $TbCl_3$ in 10 mL mili-Q-water and 0.1 m(M) of $EuCl_3$ in 10 mL mili-Q-water were added to it, and was refluxed [18] for 4 h under Ar- atm at 160° C-170° C. Finally, the solution was dialyzed by PUR-A-LYZER MEGA DIALYSIS KIT against Mili-Q water for 24 h to remove unreacted chemicals as well as excess capping agents and during the dialysis the water was also replaced at interval of 2 h.

2.5. Characterizations

To characterize last co-doped QDs, x-ray photoelectron spectroscopy (XPS) was investigated on a thick film. This measurement was done using a spectrometer supplied by Omicron Nanotechnology with the serial no. 0571 with Al- Kα radiation source under 15 kV voltage and 5 mA current. X-ray diffractometer (XRD) experiment was carried out by using RICHSEIFERT-XRD 3000P (X-ray Generator-Cu, 10 kV, 10 mA, wavelength 1.5418 Å). Microstructural studies were done by high-resolution transmission electron microscope (HRTEM). We used (HRTEM; JEOL 2100) high-resolution transmission electron microscope for microstructural analysis and EDX analysis. Raman spectra were obtained with micro-Raman JYT-6400 model with 540 nm excitation wavelength. All the photoluminescence (PL) measurements were carried out by PTI fluoromax QM-400 spectrofluorometer. During the measurement filter of 570 nm (long pass filter) had been used to avoid the appearance of the second order harmonic peak of the excitation wavelength 330 nm and to avoid the appearance of the second order grating peaks from the emission band at 403 nm in the emission spectra of different types of quantum dots. UV–visible and all the fluorescence experiments are carried out with a SHIMADZU-1601 UV–visible and Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. Time–Correlated Single Photon Counting study is performed by picoseconds NanoLED IBH-405L in an IBH fluorocube apparatus.

3. Results and discussions

3.1. Physical characterizations

Fig. 1 shows the HRTEM images of functionalized MoS_2 QDs and Eu/Tb co-doped functionalized MoS_2 QDs. The size distribution plot shows that [Fig. 1(a)] functionalized MoS_2 QDs have almost same size, i.e., 5.2 nm whereas Europium (III) and Terbium (III) co-doped MoS_2 QDs have almost average size of 5.6 nm [Fig. 1(c)]. The highly ordered lattice fringes that appeared in HRTEM images confirm the formation of crystalline MoS_2 quantum dots [Fig. 1(b)]. The lattice