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Excitation-wavelength dependent upconverting surfactant free MoS_2 nanoflakes grown by hydrothermal method

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ABSTRACT

Two-dimensional (2D) materials such as graphene and layered transition metal dichalcogenides (LTMDs) have attracted a great deal of attention by the scientific community because of its exceptional electronic, mechanical and optoelectronic properties. Unlike graphene, monolayer MoS_2 is a non-centrosymmetric material featured with a direct band gap energy of 1.9 eV that identifies the presence of strong luminescence. Here we report the growth of quantum confined MoS_2 nanoflakes with desired optical properties such as pronounced excitation wavelength dependent luminescence at room temperature. The emission luminescence was observed to shift from 560 to 704 nm with increasing excitation wavelength. In addition to the down-conversion photoluminescence, interestingly, MoS_2 nanoflakes also exhibited unusual upconversion photoluminescence. These enhanced optical properties of MoS_2 provide various exciting technological applications and thus opening up new possibilities in the field of bio-imaging, optical displays, photovoltaic light harvesting cells and other optical devices.

1. Introduction

Research interest in the isolation and fabrication of atomically thin sheets of layered 2D material graphene have enabled exploration of new 2D materials including boron nitride, transition metal dichalcogenides (TMDCs), oxides [1], hydroxides etc resembling advanced electronic structures and novel optical attributes. Particularly TMDCs exhibit a resurgence of research interest in their atomically thin 2D forms having a wide range of electronic band structures. TMDCs consists of three atom layers with chemical formula MX_2, where M represents a hexagonal plane of transition metal elements sandwiched between two hexagonal planes of chalcogen atom represented as X (S, Se, Te), the oxidation states of metal and chalcogen being +4 and −2 respectively [2]. Analogues to graphene, the weak van der Waals force between the layers facilitate the cleavage of individual layers. MoS_2 is a widely known TMDCs and an excellent graphene analogue with direct band gap (~1.9 eV), having potential applications in high performance electronic and optoelectronic devices such as transistors [3], solar cells [4], phototransistors [5], LEDs, sensors [6], complementary metal oxide semiconductor (CMOS) electronics [7,8], catalysis [9,10], lubrication [10] etc. The broken inversion symmetry of monolayer MoS_2 also paves pathway for the emerging of spintronic and valleytronic device applications.

Unlike graphene, monolayer MoS_2 undergoes transition from indirect band gap between d-orbitals of Mo and p_z-orbitals of S atoms at the Γ-point to direct band gap at the K-point of the Brillouin zone. With decreasing number of layers the indirect band gap in MoS_2 increases exceeding the direct band gap at the K-point due to quantum confinement effects. This transition from bulk indirect (Γ-K transition, 1.2 eV) to 2D direct (K-K transition, 1.9 eV) band gap semiconductor along with quantum confinement effects in layered d-electron MoS_2 leads to strong manifestation in the electronic and optical properties, naturally accounting for the emergence of strong photoluminescence (PL) behavior. The novel electronic property of MoS_2 relies on the ligand field splitting of the d-orbitals and its subsequent filling. MoS_2 mainly consists of two polymorphs: 2H-MoS_2 with a trigonal prismatic arrangement and 1T-MoS_2 having octahedral coordination. Ligand field splitting in 2H-MoS_2 leads to the formation of filled d^2_z valence band (a_1), thus making it a semiconductor and degenerate $d_{x^2-y^2,xy}$ (e') and $d_{xz,yz}$ (e″) conduction band orbitals. The layer-dependent electronic structure variations thus induce increased research interest of MoS_2 for optoelectronic applications. Optically generated stable excitons from the recombination of carriers induced by strong Coulomb interaction in atomically thin MoS_2 also plays an important role in the optical properties.

In this work, we present the size-dependent electronic characteristics induced optical properties of hydrothermally grown MoS_2

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