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Mingyang Wu

Washington University in St. Louis

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Photoluminescence quantum yield of transition metal dichalcogenide

Mingyang Wu

Abstract — Photoluminescence quantum yield (PLQY) is an important characteristic of luminescent materials. Photoluminescence (PL) is light emitted by a luminescent material after absorbing photons. Quantum yield (QY) is defined as the number of times a specific event occurs per photon absorbed by the system, Transition metal dichalcogenide (TMD) is a kind of material with the type of MX_2 . TMD is a semiconductor material, but also a two-dimensional material. Single-layer TMD has the properties of large exciton and trion binding energy, which are appropriate in the development of optoelectronics. PLQY is a good method to measure the optoelectronic properties of TMD materials.

Keywords – *Photoluminescence, Quantum yield, Transition metal dichalcogenide*

1. Introduction

Photoluminescence is a form of luminescence in which light is excited by photon absorption. This light emission occurs when matter absorbs electromagnetic radiation and re-emits the radiation. The process starts with light excitation. It means that when a substance absorbs photons and electrons move from a low-energy state to a high-energy state, the electrons of the substance are excited. After these excitations, there is a relaxation process. In the relaxation step, photons are re-radiated or emitted. The period between photon absorption and emission may vary from substance to substance.

According to the relative symmetry of the spins of the two electrons, a pair of electrons can exist in one of the two total spin states. If the two kinds of spins are in the antisymmetric configuration, the total spin of the electron pair is zero ($S = 0$), and if they are in the symmetric configuration, the total spin of the electron pair is 1 ($S = 1$). There is an antisymmetric electron spin-pair combination and three symmetrical spin-pair combinations, so the states $S = 0$ and $S = 1$ are called singlet and triplet states, respectively.

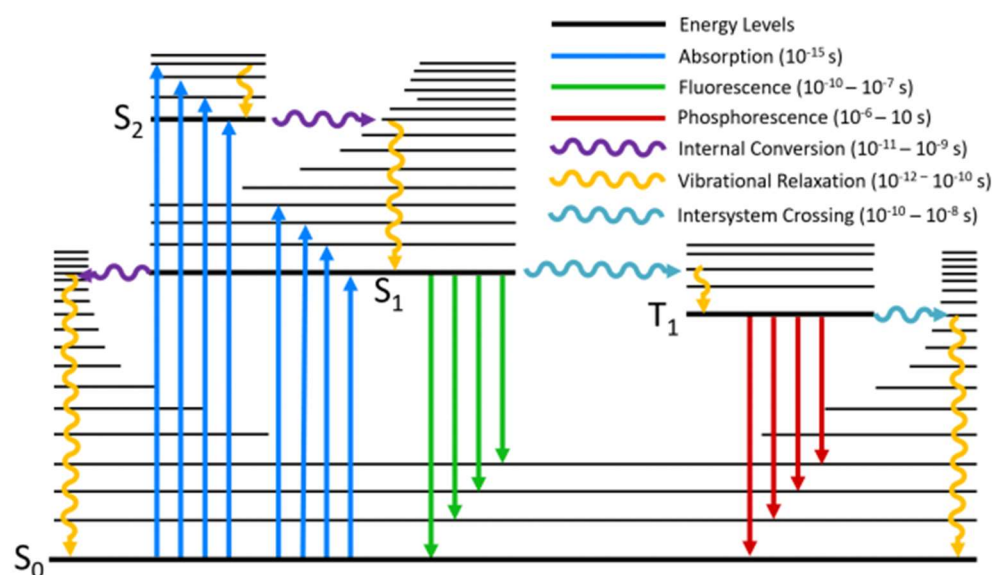


Figure 1 Jablonski Energy Diagram

When the singlet exciton undergoes a radiative transition, the S_1 state decays back to S_0 is an allowable transition (because the two states have the same spin multiplicity), resulting in rapid photoinduced transition on the picosecond to nanosecond time scale. Luminescence, this type of luminescence is called fluorescence. When the triplet exciton undergoes a radiation transition, the

T1 state decays back to the S0 state is a forbidden transition. It manifests in the slower photoluminescence, on the order of microseconds to seconds. This type of luminescence becomes phosphorescence. The emitted light color is determined by the energy difference between the ground state and the excited state[1].

The definition of quantum yield is the ratio of the number of emitted photons to the number of absorbed photons, which is an indicator of the luminescence performance of a material. When designing new materials, quantum yield is a key performance indicator.

There are two ways to measure quantum yield. The first way is the comparison method, which is generally used to measure the quantum yield in the solution. The luminescence of the molecule to be measured is compared with the luminescence of the standard molecule. Then we can obtain the quantum yield. The second method is a direct measurement, which is widely used in solution, film, and powder samples. By measuring the number of absorbed photons and the number of emitted photons, we can calculate the quantum yield of the material directly. Compared with the comparative method, the advantage of directly measuring the quantum yield of the material is obvious. It can quickly measure the quantum yield of the material, and it does not rely on known standards[2, 3].

2. Transition metal dichalcogenides

In recent years, with the development of thin-film material preparation technology, low-dimensional materials have attracted more and more attention. The chemical formula of transition metal dichalcogenide is MX_2 , where M is a transition metal and X is a chalcogenide nonmetal. These three atom layers are bound together with covalent bonds, and the atomic layers are connected by van der Waals forces. Two-dimensional layered transition metal dichalcogenide has very attractive properties, including large surface area, good electrical conductivity, and rapid heterogeneous electron transfer[4].

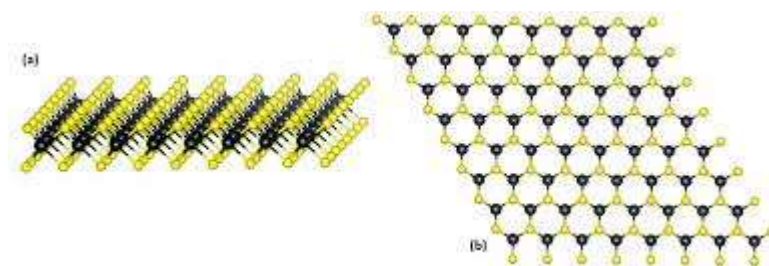


Figure 2 Structure of transition metal dichalcogenide

At present, the most reported transition metal dichalcogenide is molybdenum disulfide (MoS_2). Single-layer molybdenum disulfide has received extensive attention due to its exciting photoelectric properties and basic properties. One of the most interesting points is that as the thickness decreases, its bandgap will increase, and it transforms from an indirect bandgap semiconductor to a direct bandgap semiconductor. Bulk MoS_2 is an indirect bandgap semiconductor with a bandgap of 1.2eV, while monolayer MoS_2 is a direct bandgap semiconductor with a bandgap of 1.9eV[5].

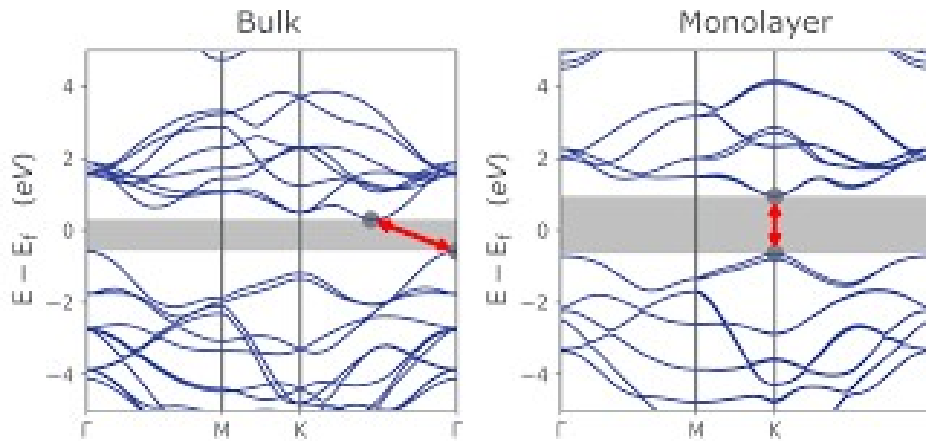


Figure 3 Band structure of molybdenum disulfide

In addition, as the thickness decreases, PLQY has increased by four orders of magnitude. The single-layer MoS_2 has a high specific surface area, so it has a high light absorption efficiency. It can absorb 10% of incident sunlight, which is an order of magnitude higher than Si and GaAs. Although MoS_2 is a good light-absorbing material, its PLQY is still relatively low. The low PLQY is due to structural defects and off-stoichiometry in MoS_2 . [5, 6] The formation energy of a single layer of MoS_2 is very low, so there are usually several S vacancies in the material. These S vacancies usually act as n-type dopants and act as non-radiation. The recombination center reduces the radiation recombination process [7]. In addition, the carrier concentration in MoS_2 is relatively large, and the Auger recombination in the system is dominant, which reduces the photoluminescence quantum efficiency. The increase of the carrier density will increase the formation of trion, which further hinders the radiation recombination process of neutral excitons [8].

3. TMD photoluminescent materials

Kishore K. Madapu et al. used atmospheric pressure CVD to grow 1L- MoS_2 samples on SiO_2/Si substrates, using MoO_3 and S as precursors, maintaining 160°C and 700°C at both ends of

the reaction chamber, respectively Heating, the temperature in the middle is 200°C, and a large area of MoS₂ film is formed in the chamber. Their experiments have proved that the PLQY of a large-area MoS₂ is at least an order of magnitude larger than that of a small-area MoS₂. It is because the laser irradiation makes The local temperature rise is significantly reduced, but due to effective heat dissipation, the local heating effect of the large-area film is greatly reduced. Through Stokes and anti-Stokes Raman analysis, under the same laser power, the local elevation of the small-area film (~33μm²) is about 94K higher than that of the large-area film (~5778μm²)[8].

Jingyuan Wu et al. used the ultrasonic peeling method. First, they used ultrasonic waves to generate several bubbles, and the flow shear force was generated through the local high temperature and high pressure and rapid liquid jet caused by bubble collapse. At the same time, with the presence of standing waves in the solution, the MoS₂ nanostructures were stripped from the MoS₂ bulk structure. Afterward, alkali metal ions were added to the solution to promote the exfoliation of more nanosheets, and MoS₂ quantum dots were obtained. After excitation with NaOH solution, PLQY increased from 0.99% to 4.99% under 440nm excitation[9].

Matin Amani et al. used an oxidizing organic superacid bis(trifluoromethane) sulfonamide (TFSI) to treat the MoS₂ monolayer film. After TFSI treatment, the intensity of the emission peak increased by 190 times, but the overall spectrum shape did not change. The magnitude of PLQY depends on the quality of the original single layer. The peak efficiency of PLQY of MoS₂ generated by the mechanical peeling method is 1%. After using TFSI processing, the maximum value of PLQY exceeds 95%, and the longest observation time exceeds 10.8 nanoseconds, which will play an important role in the development of high-efficiency light-emitting diodes, lasers, and solar cells in the future[10].

Hyungjun Kim et al. used Ar/H₂ as a carrier gas to grow WSe₂ single-crystal domains and WSe₂ single-layer films on a quartz substrate by low-pressure CVD. First, the substrate was cleaned by sonication in acetone and isopropanol for ten minutes, and the cleaned substrate was installed downstream of the furnace. In the fabrication of micron-sized WSe₂ samples, a ceramic boat of a mixture of KBr and WO₃ with a mass ratio of 1:2 was placed next to the substrate, and KBr was used as an accelerator. The tube furnace is evacuated to about 1 Pa, the carrier gas is introduced until the standard atmospheric pressure is reached, and the furnace is raised to 700~850°C at a rate of 35°C/min and maintained for about 20 minutes. In the fabrication of WSe₂ single-layer film, a

ceramic boat with a mass ratio of 1:1 was used instead and placed next to the substrate, and the growth time was changed to 45 minutes. In their experiments, the PLQY at low injection levels was 60%, and the PLQY at high injection levels was 12%, which is much higher than the previously reported value[10].

	Product	Method	Quantum Yield
Kishore K. Madapu et al	MoS ₂ single layer	CVD	1.8%
Jingyuan Wu et al.	MoS ₂ quantum dots	Ultrasonic peeling	4.99%
Matin Amani et al.	MoS ₂ single layer	TFSI treatment	95%
Hyungjun Kim et al.	WSe ₂ single-crystal domains	Low-pressure CVD	60%

Table 1 The methods already published

4. Conclusion

This article first introduces the process of photoluminescence and introduces the definition of quantum yield and two methods of measuring quantum yield. Afterward, we introduced the properties of transition metal dichalcogenides and emphasized the photoluminescence properties of transition metal disulfides. Subsequently, we introduced four preparation methods of transition metal dichalcogenides. Including two preparation methods of molybdenum disulfide monolayer films, a preparation method of molybdenum disulfide quantum dots, and a preparation method of tungsten selenide. Matin Amani et al. used the molybdenum disulfide prepared by TFSI to obtain a quantum efficiency as high as 95%, and several other methods also achieved relatively high quantum efficiency. Through summary, we found that using strong acid or alkali treatment, or using the CVD method to generate thin films, can improve the photoluminescence quantum yield of transition metal dichalcogenides.

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