0D quantum dots @ 2D materials multi-structure tin monosulfide for high-performance visible light photocatalyst

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Environmental pollution from chemicals used in industrial processes is a major concern, and usage continues to increase, mainly in developing countries. Among them, water pollution has become an increasingly important environmental pollution factor with industry development and a fundamental cause that can lead to soil pollution. Methylene blue (MB), a representative cationic thiazine dye widely used in various fields, including chemical and biological industries, can cause fatal health problems including vomiting, nausea, extreme sweating, eye irritation, and mental disorders. These organic synthetic dyes are the most widely used in the pharmaceutical, leather, textile and general manufacturing industries. Synthetic dyes are toxic even at low concentrations and must be removed from industrial wastewater before discharge into aquatic systems. Over the past few decades, many researchers have been trying to find various methods and techniques for removing these dyes from industrial wastewater. Although adsorption, coagulation, UV degradation, oxidation and reduction treatments are commonly used to remove dyes, most of these techniques are costly and pose secondary hazards including toxic and hazardous chemicals. However, the decomposition of organic dyes through photocatalysis does not generate secondary chemicals and is harmless to nature, which is convenient for industrial use. The photocatalytic degradation of methylene blue has long been studied using a variety of materials.

In recent years, black phosphorus(BP), which has been spotlighted as a new two-dimensional material, has attracted attention as a material that can satisfy both the advantages of graphene and TMDC. Black phosphorus has a direct bandgap with thickness and its excellent electrical and optical properties make it an attractive material for a wide range of applications. Phosphorene is advantageous for optical applications because the band gap depends only on the number of layers. In addition, phosphorene demonstrated high carrier mobility, layer-dependent photoluminescence (PL) and anisotropic behavior. In addition, Kim's group recently showed that the crystal structure of black phosphorus can be controlled by bipolar-like spin semiconductors. Due to its high carrier mobility, it is used as a semiconductor material such as solar cells, electric devices, and batteries, and is also used in applications such as sensors and photoelectric devices. However, it is the biggest obstacle to practical use that shows rapid deterioration of properties due to low stability after exfoliation. In order to improve this stability, various methods such as introduction of protecting layer and surface substitution method have been studied, but there are still difficulties in commercialization.

Thus, a 2D material that can be proposed as a series of alternatives is Tin monosulfide (SnS). This material is similar to BP and has a curved honeycomb structure similar to that of BP, has an adjustable bandgap according to thickness, electrical and optical properties, and has high stability. It has anisotropy with a curved honeycomb structure like BP, and has high chemical stability due to the combination of cation and anion layers in the orthorhombic crystal structure of Sn and S (Lee et al., 2020). In addition, unlike the high-priced BP, it has advantages in commercialization as it is inexpensive and easy to synthesize. In photocatalytic reactions that take place in a moist environment, high stability to water can be a great advantage.

In this study, the optimal photocatalytic reaction band was designed by combining 2D nanosheet type SnS and quantum dot type 0D SnS with shape control to adjust the band gap for photocatalytic reaction. Quantum dot-type materials exhibit unique physicochemical properties that can be confirmed in materials with a size of several nm, such as quantum confinement effects. This leads to fast charge separation and increased photocatalytic efficiency due to many reaction sites. Quantum dots absorb light with a relatively wide bandgap to separate charges, and 2D sheets act as aceptors to inhibit recombination. The recombination reaction of electric charges is a very important factor in the performance of the photocatalyst. The synthesized material exhibited high stability due to its high crystallinity and strong resistance to photocorrosion. Through this bandgap control technology, it can be widely used in other photocatalyst fields and is promising as a study for materials that can replace BP in other applications.

Figure 1 shows a structure in which bulk black and tin monosulfide (SnS) atoms are covalently bonded to form a special wrinkled 2D structure. Both BP and SnS have a similar structure and are direct-gap semiconductors whose bandgap can vary depending on the number of layers. Recent theoretical and experimental studies have shown that BPs are good candidates for realizing novel optoelectronic, electronic, thermoelectric and nanomechanical devices due to these band properties. The unit cell of the two materials is rectangular, and the long axis is called the armchair direction and the short axis is called the zigzag direction, and the direction can be defined accordingly in the Brillouin zone.

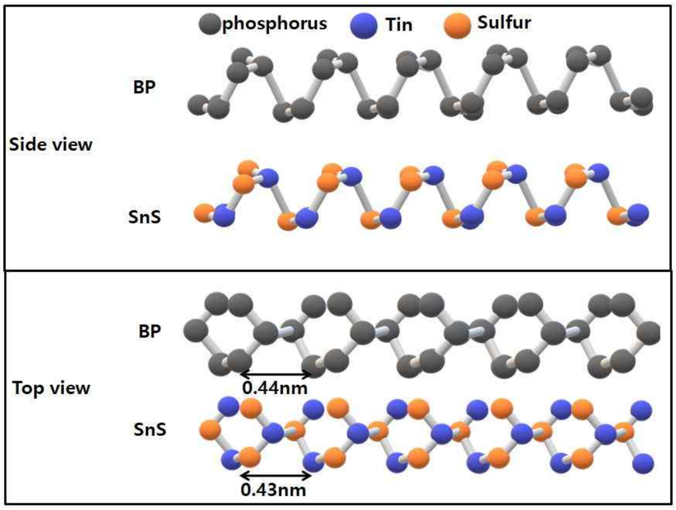

Figure 1: Black phosphorus and tin monosulfide's side view and top view of layer

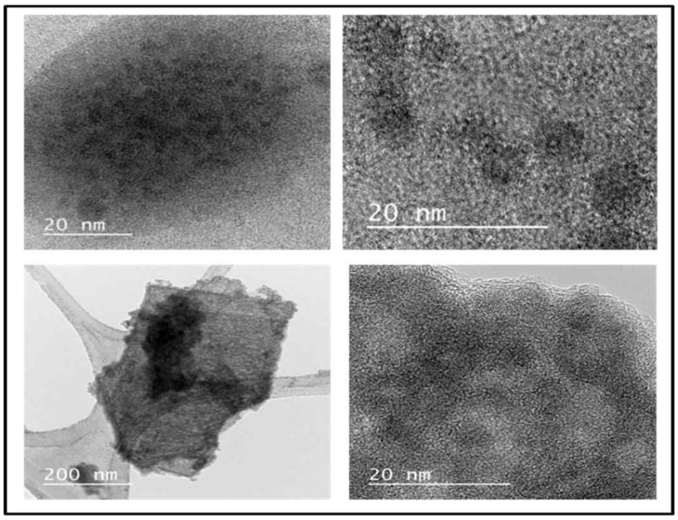

Figure 2: TEM image of SnS in the form of synthesized Quantum dots (top), 0D/2D SnS (bottom).

In this study, using the hydrothermal method, a SnS material with a 2D nanosheet structure and a 0D quantum dots complex structure was successfully synthesized. It was possible to control the growth of SnS by adjusting the pH during the synthesis process, which was confirmed as a normal tin monosulfide orthorhombic crystal structure by measurements such as TEM, EDS, XRD, and Raman. This has been successfully proposed as a way to solve the problem of oxidation stability after exfoliation, which is the main issue of BP materials with high crystallinity and material stability. In addition, based on this stability, it showed excellent durability with high efficiency in photocatalytic reactions in water. In addition, the bandgap that changes according to the thickness and dimension is designed according to the photocatalytic reaction with shape control technology. By arranging two shapes with different band gaps, the photocatalytic efficiency was increased by preventing recombination after charge separation. This mechanism was analyzed by the Time-resolved Photoluminescence method. Tin monosulfide different dimension shape has a different band gap, so it can act as a donor / acceptor like the heterojunction. This increases the lifetime and reduces the recombination rate. This is about a fourfold increase in rate constant k compared to photocatalysis with a single SnS material.In addition, the photocatalytic performance was maintained even after 10 reuses with high stability in contrast to black phosphorus. Designing and fabricating bandgap energy-matched nanocomposite photocatalysts may provide a fundamental direction to solve future clean energy challenges. This study is an important step towards exploring the interesting properties of the BP analogs, 2D SnS and 2D monochalcogenides.