Investigation of MoS2 layered nanostructures for photocatalytic applications

（課程博士・様式７）（Doctoral qualification by coursework, Form 7）

学 位 論 文 要 旨

Abstract of Doctoral Thesis

専　　攻：光・ナノ物質機能　　氏　名：マニ　サバリナザン

Course：Optoelectronics and Nanostructure Science　　Name：Mani Sabarinathan

論文題目：光触媒応用のための二硫化モリブデン層状ナノ構造に関する研究

Title of Thesis：Investigation of MoS_2 layered nanostructures for photocatalytic applications

論文要旨：

Abstract：

Nanotechnology is a new field of research for fabrication of devices based on the enhanced properties of materials in the realm of 1 - 100 nm. Semiconductor nanostructures are expected to exhibit enhanced optical properties when compared to bulk semiconductors because of quantum confinement. These semiconductor structures have been widely used in various applications such as optical sensors, photocatalysts in environmental protection, flat panel displays, storage devices, blue laser diodes, light emitting diodes. Among them, semiconductor photocatalyst nanostructures are very closely linked with the technical assessments of environmental cleanup. A remedial action provides important inputs to the environmental assessment on technology design and dimensioning, which are expected short remediation time and high remediation efficiency. A remediation technology removes a local contamination and contribute to environmental purification on the local, regional and global scale. Water is the most basic and most essential compound of all living processes in our water planet. Despite many attempts to stop the destruction and pollution of water resources, humans' impact on the natural cycle of water make irreparable risks in this area and it requires a consideration on the necessity of the use of new methods to prevent contamination of water resources. Wastewater compounds may be physical, chemical or biological, and cause environmental impacts including changes in aquatic habitat and its special structure, and the change in biodiversity and water quality.

The synthesis of nanoparticles with uniform size and morphology is one of the most significant challenges in nanotechnology. For semiconductor nanoparticles, different emission wavelengths are obtained for different particle sizes, and so the control of particle size is very important for these systems. The traditional approaches to prepare nanoparticles involve co-precipitation, deposition - precipitation, ion exchange, impregnation, successive reduction and calcinations, etc. These approaches, however, experience lack of control over size, shape and stability of the produced nanoparticles. It is well known that without surface active agents, a narrow size distribution is hardly achieved. Such controllability or processibility of size, shape and surface properties are important in delineating the size effect in nanostructured catalysis. An ideal nanoparticles catalyst system should be not only catalytically accessible, but also morphologically stable or controllable. This can be achieved by surface-capping approaches.

In the present work, Molybdenum disulfide (MoS_2) layered nanosheets were synthesized by the hydrothermal method. Citric acid was used as an organic ligand to obtain the monodispersed layered MoS_2

nanostructures. The effect of citric acid on the formation and functional properties of the layered MoS_2 nanostructures was investigated. The X-ray diffraction patterns (XRD) revealed the formation of a hexagonal crystal structure of MoS_2. Significant peak shift was observed for the interaction of citric acid and Mo in the core level spectra of X-ray photoelectron spectroscopy (XPS). Citric acid-free hydrothermal growth resulted in the formation of micron-sized MoS_2 spheres, whereas citric acid-assisted hydrothermal growth resulted in the formation of well dispersed MoS_2 layered nanostructures, confirmed by morphological analysis. However, the highest concentration (0.05 M) of citric acid resulted in the formation of aggregated layers. The obtained MoS_2 nanostructures were used as photocatalysts to decompose methylene blue (MB) as a model pollutant. The obtained results showed that the MoS_2 layered nanosheets could effectively decompose the organic pollutant. The MB absorption peaks completely disappeared after 24 min of irradiation when using the nanosheets synthesized with a citric acid concentration of 0.04 M. The effect of pH on the MoS_2 nanosheets was studied, and 96 % MB degradation was observed at pH 12 after 2 min of visible-light irradiation.

2D layered molybdenum disulfide (MoS_2) and MoS_2/TiO_2 nanocomposite were synthesized by the hydrothermal method. The effect of TiO_2 concentrations on the formation of MoS_2/TiO_2 composites and functional properties were investigated. XRD revealed the formation of hexagonal and anatase structure of MoS_2 and TiO_2, respectively. XPS confirmed the presence of Mo and Ti interaction by significant peak shift. Morphological analysis revealed the formation of TiO_2 grown on the surface of MoS_2 nanosheets. The photocatalytic degradation of methylene blue (MB) in the aqueous suspension was employed to evaluate the visible light activity of as-prepared composite photocatalyst. The MB absorption peaks completely disappeared after 12 min with 99.33 % of degradation under visible light illumination at TiO_2 of 0.005 M. It was found that hydroxyl radical (•OH) played the important role for the degradation of MB under visible light illumination. The possible charge transfer mechanism was proposed.

Rare earth metal doped layered 2D molybdenum disulfide (MoS_2) nanostructures were synthesized by the hydrothermal method. XRD revealed the hexagonal formation MoS_2 nanostructures. XPS confirmed the presence of Ce ions in MoS_2 nanostructures which resulted significant peak shift. Morphological analysis of field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images revealed the layered formation in MoS_2 nanostructures. The effect of Ce ions in MoS_2 nanostructures for photocatalytic activity was investigated and the photocatalytic degradation of methylene blue was evaluated under visible light irradiation. The methylene blue absorption peaks completely disappeared after 12 min with 99.39 % of degradation under visible light irradiation at Ce of 5 mM concentration. The introduction of cerium (Ce) ions into MoS_2 showed increased photocatalytic activity. Cerium ions attributed to the improvement of formation of reactive oxygen species owing to the presence of Ce^{3+}. The hydroxyl radical (•OH) played the important role for the degradation of methylene blue under visible light irradiation. The possible charge transfer mechanism has been proposed.

The above results clearly confirm that the well-defined 2D layered MoS_2 nanostructures was effective for the photocatalytic degradation of organic pollutant under visible light irradiation.