Journal of The Electrochemical Society, **166** (8) H263-H271 (2019)
0013-4651/2019/166(8)/H263/9/$38.00 © The Electrochemical Society

Phase Engineering from 2H to 1T-MoS_2 for Efficient Ammonia PL Sensor and Electrocatalyst for Hydrogen Evolution Reaction

Levna Chacko,[1] Pankaj Kumar Rastogi,[2] and P. M. Aneesh [1,z]

[1]*Department of Physics, Central University of Kerala, Tejaswini Hills, Periye, Kasaragod, Kerala 671316, India*
[2]*Tata Institute of Fundamental Research-Hyderabad, Gopanapally Village, Hyderabad 500 107, India*

In the recent years, phase transitions in MoS_2 from 2H to 1T has gained considerable research interest that finds significant technological applications. This paper describes the development of active 1T MoS_2 exhibiting metallic behavior from the semiconducting 2H MoS_2 by simple two-step hydrothermal method without adding any additional atoms. This strain induced synthesis method allows the modification of the crystal phase and facilitate the electron transfer with reduced resistance of 89 Ω. We studied the formation of 1T MoS_2 nanostructures using X-ray diffraction, spectroscopic and microscopic scientific tools. The metallic 1T phase is found to exhibit markedly high optoelectronic properties demonstrating an excitation wavelength dependent down-conversion and up-conversion photoluminescence. The large surface area, tunable bandgap, high electron mobility and increased active sites of 1T MoS_2 elucidates a viable designing of optical photoluminescence ammonia sensing. Finally, we investigated the integration of 1T polymorph into an efficient electrocatalytic hydrogen evolution system to compare their catalytic activity with that of 2H MoS_2. 1T MoS_2 is found to exhibit a low onset potential of 240 mV vs RHE than the 2H phase with a comparatively high onset potential of 550 mV vs RHE. The superior activity of 1T MoS_2 owing to the abundant catalytic edge sites are critical for global production of clean and renewable energy sources.
 [DOI: 10.1149/2.0071908jes]

Manuscript submitted January 16, 2019; revised manuscript received March 18, 2019. Published April 24, 2019.

The phase transitions in MoS_2 has attracted intriguing research interest due to the far exceeding unique potential applications of these low dimensional direct bandgap material. MoS_2 exhibits mainly three polytypes based on the stacking order: octahedral (1T phase, D_{3d} point group), trigonal prismatic (2H phase, D_{3h} point group) and 3R polytype with a space group of C_{3v} (R3m). 2H-MoS_2 is semiconducting and thermodynamically stable having hexagonal symmetry with two S-Mo-S layers built from edge sharing MoS_6 trigonal prisms, whereas 1T- MoS_2 having metallic behavior is composed of a single S-Mo-S layer consisting of edge sharing MoS_6 octahedra with tetragonal symmetry. The ability of MoS_2 to crystallize in 2H phase and transit into 1T phase upon distortion or intercalation is worth demanding for geometrically tailoring the hydrogen production due to increase in the exposure of active sites. Unlike the trigonal 2H polymorph, the octahedral structure of 1T MoS_2 possesses proliferated active edge sites, increased surface area and electron mobility. The phase transition from 2H to 1T thus has considerable attention as an electrocatalyst in the hydrogen evolution reaction (HER).

Ongoing pursuit of hydrogen as a promising high gravimetric green energy carrier created a great renaissance in the present exhaustible hydrocarbon economy due to its abundance, accessible synthesis and non-polluting behavior. Electrochemical and photochemical water splitting method is an effective strategy replacing hydrogen production from fossil fuels. In this effort, electrocatalysts play great role in hydrogen evolution reaction (HER, $2H^+ + e^- = H_2$), reducing Gibbs free energy which is a measure of overpotential and thereby enhancing energy efficiency. Noble metals such as platinum, iridium, rhenium etc are most effective HER catalysts having high efficiency. But the high cost and low availability still remains as challenging factor thus inhibiting their application. Identification of new cost effective and abundant HER electrocatalyst is a momentous requirement in advanced technology of production of hydrogen, an environment-benevolent energy carrier.

Having a hydrogen binding energy approximate to that of rare metals like platinum ($\Delta G \sim 0$) in the volcano plot obtained from density functional calculations, MoS_2, a widely used catalyst for hydrodesulfurization in petroleum refining displays excellent activity in HER. MoS_2 is also an excellent highly competitive earth-abundant catalyst and considered as a potential substitute for rare and expensive catalysts such as Pt, as electrocatalyst for hydrogen oxidation in fuel cells. Studies demonstrates that dominant catalytic sites of MoS_2 is located along the sulfided Mo-edges, while basal planes remain inert due to weak H-binding on basal planes.[1–3] However, the low solubility, poor conductivity, weak electrochemical durability and reduced surface area make it greatly challengeable for practical and potential application in HER performance. Therefore, it is required to increase the number of active sites, activity of catalytic sites, electrical conductivity and durability etc by effective tuning and engineering of catalytic sites and electronic conductivity. Prior to, the disulfide terminated edge of MoS_2 has been perceived as the active site for HER. Enhancing the number of active sites (sulfur terminated Mo-edge) by altering the atomic or electronic structure of the MoS_2 nanostructures so as to increase the H binding ability have remained a central concern for methodical and energy-saving hydrogen production.

Voiry et al. reported the excellent electrocatalytic activity of chemically exfoliated MoS_2 nanosheets for hydrogen production due to dominant metallic 1T phase in the exfoliated samples.[4] An electrochemical Li intercalation technique reported by Wang et al.[5] demonstrated better HER catalytic activity through continuous tuning of oxidation state of Mo and transition of 2H semiconducting to metallic 1T phase of MoS_2. Gao et al.[6] investigated the effect of phase transition from semiconducting 2H-MoS_2 to metallic 1T-MoS_2 and further to 1T'-MoS_2 phase for HER by density functional theory. Transformation of the basal plane from 2H to 1T' phase upon lithium intercalation was demonstrated by Chou et al.[7] which resulted in a lowering of Gibb's free energy of hydrogen adsorption (ΔG_H) to 0.18 eV for 1T' MoS_2 making it a futuristic catalyst. Kang et al.[8] demonstrated the photocatalytic enhancement of 2H to 1T phase transformed MoS_2 due to plasmonic hot electrons doping and the stress that caused from the Au@Ag nanorattle deposited on the MoS_2 surface. Different methods have been employed to enhance the active sites of MoS_2, which include chemical, mechanical and liquid exfoliation techniques, intercalation of metal ions etc.[4,9,10]

Apart from the catalytic properties, 1T MoS_2 also find potential applications in industries, environment monitoring, military, agriculture, medical fields etc as an effective sensor. Sensing of toxic gas molecules is more critical and important in these fields. Firstly, the increased surface area, chemical and thermal stability of nanostructured materials marks its application as sensors with excellent sensitivity upon the exposure of various analytes. Secondly, the sensing behavior also depends on the adsorption and desorption of the gas molecules, which act as charge acceptors or donors or neutral molecules. Gas sensors based on graphene,[11] graphene oxide,[12] MoS_2[13] etc have been already developed. Here, we investigated the photoluminescence (PL) sensing property of 1T MoS_2 toward various toxic compounds. Detection and monitoring of organic pollutants and toxic compounds are essential for environmental management and important in medical, food, chemical

[z]E-mail: aneeshpm@cukerala.ac.in