VIETNAM NATIONAL UNIVERSITY – HCMC
Ho Chi Minh University of Technology

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DISSERTATION INFORMATION

Title: **Nanostructured materials based on Molybdenum disulfide (MoS_2) and carbon nanotubes (CNTs) for lithium-ion batteries (LIBs) and hydrogen evolution electrocatalysts**

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Major: **Materials Engineering**

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Summary

This doctoral work studies MoS_2 and MoS_2/CNT nanostructures and also discusses how structural design can successfully address their challenges in lithium-ion batteries and electrocatalysts. Recent advances in nanoparticle synthesis, nanostructure design, and composite fabrication are summarized and discussed, as well as their impact on electrochemical performance. Additionally, the remaining challenges and opportunities for further improvement are discussed.

This study reviews the development of the microwave method, introduces the reaction mechanism, and focuses on the practical application of this method. The microwave-assisted synthesis of inorganic nanostructures in MoS_2 in polyols is also discussed. MoS_2 nanoscale prepared in the presence of a strong microwave absorber is rapidly formed in minutes, yielding clean reactions with different morphologies and sizes. In this work, a microwave-assisted technique was successfully used to produce the hybrid material 1T/2H-MoS_2. The highest 1T concentration reached was 84.5% compared to the 2H phase. It is believed that the hybrid nanostructures display superior electrochemical performance due to the metallic 1T phase's enhanced electrical conductivity.

Apart from that, the research provides a general picture of the employable materials synthesis processes. Many review articles have been published on the microwave-assisted synthesis of nanostructured materials. Microwave heating can affect the reaction rate by shortening the reaction time. The rapid heating rate and/or "superheating" may change the reaction mechanism. The scaling up of microwave-assisted chemical reactions is very important for industrial scale production and applications of nanostructured materials. In this study, microwave heating was also demonstrated to be efficient in wet chemical reactions for the synthesis of MoS_2 and MoS_2/CNT nanocomposites.

The formation of the MoS_2/CNTs nanocomposite in the forms of crystalline and amorphous structures was achieved using the two dispersion processes for functionalized MWNTs, indirect two–pot dispersion (I2PD) and direct two–pot dispersion (D2PD), respectively.

The conditions for optimizing synthesis of crystalline MoS_2/CNTs are as follows:

- f-CNTs (10 g/L) amount: 4mL
- Time of reaction: 60 mins.
- Solvent amount: 240 mL
- Microwave power: 240 W
- Temperature of ultrasonication: 60 ^{o}C

The conditions for optimizing synthesis of amorphous MoS_2/CNTs are as follows:

- Microwave power: 560 W
- Time of reaction: 30 mins.
- Temperature of ultrasonication: 60 °C
- f-CNTs amount: 10 mg.
- $\sum m_{(AMH+TU)} : V_{EG} = 0.06$ g/mL

The Taguchi experimental method also determined the effect of factors on the efficiency of MoS_2/CNTs material synthesis. The results reveal that microwave power has the most impact on crystallinity ‘higher-is-better’ and reaction time has the greatest impact on the Tafel slope “lower-is-better”.

Using linear sweep voltammetry (LSV) at a scan rate of 1 mVs^{-1}, the catalytic potential of MoS_2/CNTs nanocomposites for the HER reaction was investigated (Tafel plot). Amorphous MoS_2/MWNTs exhibit catalytic capability and stability in the -220 ÷ -230 mV (vs. NHE) range, with a current density of -8.94 mA/cm^2 (V = -350 mV vs. NHE) and a Tafel slope of 102 mV/dec.

A microwave-assisted technique was used to successfully produce a nanocomposite of crystalline MoS_2/CNTs for use as an anode material in lithium-ion batteries. The discovery that the crystalline MoS_2/CNTs (LA-MSC-opt) electrodes retain their performance after 54 cycles at a scan rate of 100 mV/s demonstrates that the material is capable of stabilizing the charge-discharge capacity over an extended period of time without structural deterioration. The crystaalline MoS_2/MWNTs anode has an initial capacity of 1.200 mAh/g, which decreases to 762 mAh/g after 60 discharge-charge cycles. The lithiation and delithiation of Li^+ and the reversible nature of the anode were clearly demonstrated by cyclic voltammograms.

The new ideas of the research (Novelty)

- A novel scalable one-step microwave heating approach is developed to obtain a high rate of metallic 1T-MoS_2 in the 1T/2H hybrid phase of MoS_2 to enhance the catalytic hydrogen evolution reaction (HER).
- Using microwave heating to control the 1T/2H ratio in polyol solvents, including ethylene glycol (EG), mixed ethylene glycol and glycerol, glycerol, and ethylene glycol with a small amount of water has not been reported before. This work discusses the effects of various polyol solvents on the synthesis of MoS_2 hybrid phase under microwave heating.
- It is worth noting that pure 1T-MoS_2 has a metastable state, which severely limits its application. The successful synthesis of hybrid phase 1T/2H-MoS_2, in which the metastable 1T phase can be stabilized by interaction with the 2H phase, significantly increasing its catalytic activity, provides a scientific foundation for using hybrid phase MoS_2 to replace Platinum (Pt) in the electrochemical hydrogen evolution reaction (HER).
- Additionally, the synthesis of crystalline and amorphous MoS_2/CNT nanocomposites in polyol solvents using microwave heating has not been extensively studied. MoS_2/CNTs, with their crystalline structure, exhibit superior electrochemical performance in lithium-ion battery (LIB) applications, whereas amorphous MoS_2/CNT materials demonstrate catalytic activity in the hydrogen evolution reaction (HER).

Major contributions of the thesis

- This thesis establishes a critical foundation and initiates a new research direction in catalysis, energy storage, and conversion based on MoS_2 nanostructured materials and carbon nanotubes in Vietnam in general, and VNU-HCM in particular, in order to keep pace with the global trend of advanced materials research.
- The ability to control the structural morphology and particle size of hybrid structures 1T/2H-MoS_2 and MoS_2/CNTs nanocomposite using microwave energy have crucial scientific significance in choosing this method to create MoS_2, MoS_2/CNTs nanomaterials in particular and many other nanostructured materials in general. With the outstanding advantages of microwaves, such as time and energy savings, the reaction at air pressure can produce a large number of synthetic products (gram scale), which is much higher than other hydro/solvothermal methods, which is vital in speeding up laboratory research.
- Experiment data have a high reference value, contribute to the scientific database in the field of one-dimensional and two-dimensional nanomaterials, and open up valuable alternative research methods in material technology materials for energy storage and conversion applications, such as those found in HER and LIBs.

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