DISSERTATION INFORMATION

Title: **Synthesis, structural characterization, optical and electrical properties of MoS_2/graphene nanocomposite.**

Major: **Materials Engineering**

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Summary

Graphene, molybdenum disulfide (MoS_2) materials and their composite forms are currently of great interest to domestic and international researchers because of their two-dimensional (2D) layered crystal structure, atomically-thin (atomic/several atomics thickness), excellent electrical conductivity, large specific surface, semiconductor and magnetic properties, etc. These unique characteristics make them highly favorable for applications in electronics, sensors (gas, light), energy storage and conversion devices (capacitors, supercapacitors, solar cells), which is the foundation of the cyber physical network system – the infrastructure of the internet of things (IoT), especially in the inevitable trend of the current industrial revolution 4.0 and clean energy transformation.

This dissertation is focused on the hydrothermal synthesis of MoS_2/graphene nanocomposite (MoS_2/C NC) and the study of the impact of key experimental parameters on microstructures, morphology that define their electrical, electrochemical and optical properties. Thereby, determining the appropriate parameters to fabricate MoS_2/C NC systems with high conductivity and broad band luminescence for energy storage device or optoelectronic applications. The systematically investigating, and carefully evaluating the synthesized nanocomposite systems by employing advanced material analysis techniques such as XRD, Raman, FESEM, TEM, HRTEM, STEM-HAADF, XPS, PL, UV-Vis, EIS, CV, combined with the fabrication process of nanogap devices by *e*-beam lithography, dielectrophoresis (DEP), Volts – Ampere characteristic measurement (I – V 4-probes semiconductor technique) help to evaluate the formation and crystallization process, crystalline structure, surface morphology, chemical composition, electrical, electrochemical and optical properties and determine the suitable parameters to synthesize nanocomposite materials with designed microstructure and properties.

The results of this work show that MoS_2/C NC systems have been successfully synthesized at 230 °C, in ~2 h, from graphene oxide (GO) dispersion (1.0 mg L^{-1}, ~84.73% C) and Mo^{4+} and S^{2-} sources. The molar ratio (Mo^{4+} : C) and pH are controlled

at ~(1.46 : 1) and ~7.2–8.8, respectively. Two-dimensional (2D) MoS_2 petal-liked crystals, thickness of ~0.63–3.69 nm was in-situ grown on graphene sheets forming “sandwich”, “layer-by-layer”, “vertical-stacked” and “anchored” nanocomposite structures. The underlying crystallized mechanism of 2D MoS_2 on GO undergoes four regimes that could be addressed as, i) a diffusion-limited process combined with the interaction of molybdate ions with precursors, ii) hydrothermal reaction between molybdates and sulfur ions at the rich-active sites GO matrix to form nucleus, iii) the growth instability characteristic of a MoS_x in unsaturated hydrothermal medium, and iv) the phase transition of MoS_x polymorphs to 2D MoS_2 nanostructures. In the context, the important role of graphene oxide is highlight as a suitable platform for growing such 2D MoS_2 nanostructures.

The MoS_2/C NC systems dominating with ultrathin (~1–6 monolayers) metallic 1T-MoS_2 phase on graphene, have high electrical conductivity (G ~ 0.180–98.815 μS) and large specific capacitance (C_{sp} ~ 122.20 F g^{-1}) were successfully synthesized at temperature and (Mo^{4+} : C) molar ratio below ~230 °C and ~(1.5 : 1), respectively. Meanwhile, nanocomposite systems with semiconductive 2H-MoS_2 phase were obtained at temperatures above 230 °C exhibit strong optical absorption (~82 %) and wide luminescence with large band gap of ~1.31–2.34 eV. The underlying mechanism of improving the conductivity of MoS_2/C NC originates from the metallic boundary structure forming at the contact layers between the dispersed phase 1T-MoS_2 and the graphene matrix that facilitate its highly conductive sp^2 hybridization restructured, and increased the charge carriers’ mobility. While, the donor-acceptor electronic structure characteristic at the ultrathin 2D semiconductive 2H-MoS_2 phase and graphene interface breaks the band symmetry of 2D MoS_2, forms mid-gap bands and allows the intralayer photoexcited electron-hole generation, excitons transition or electron tunneling mechanisms and exceptional photoresponse in various types of MoS_2/C NC. Such structure broadens the optical band gap, enhances the nonlinear optical property, strong optical absorption and broad band photoluminescence of dispersed MoS_2 phase in MoS_2/C NC.

The results of this dissertation also suggest that the metallic (1T) to semiconductive (2H) phase transition and large band gap with mid-gap bands structure of 2D MoS_2 can be engineered by controlling reaction temperature and pH value through the synthesis of MoS_2/C NC. The ability to tune the band gap and nonlinear optical property as well as the memristive of the 2H-MoS_2 semiconductive phase which originates from the double-layer electrochemical storage mechanism of the Mo atomic layers and the MoS_2–graphene contact layer, that make them promise for applications in broad band electromagnetic wave absorbers, optoelectronics and memristors. The proposed synthetic approach in this dissertation can also be applied as a reliable and scalable strategy to fabricate MoS_2/graphene nanocomposite and various functional materials with tunable structures, electrical and optical properties.

The successful fabrication of MoS_2/C NC by facile hydrothermal method with controllable microstructure, band gap, electrical and optical properties by engineering experimental parameters, thereby, contributing to the scientific research and industrial applications of nanocarbon-based next-generation materials in Vietnam, and catching up with in the world's hottest advanced functional materials research trends.

Novelty and key contributions of this dissertation

(1) Establishing a procedure to synthesize MoS_2/C NC with high electrical conductance, large specific capacitance and wide optical band gap by a simple hydrothermal method with less harsh reaction condition, easy to control performance of products based on their practical applications.

(2) Proposing an effective method for restoration the sp^2 hybridization domain of chemically synthesized graphene from rich-defect structure of GO sheets, and improving its high electrical conductance by in-situ anchoring 2D MoS_2 crystals via the donor-acceptor structure at the GO defects sites. Concurrently, suggesting a facile method to fabricate MoS_2/graphene nanocomposite systems with crystalline structures and such properties as metallic or semiconductor that can be fully engineered by controlling the reaction temperature through the metallic (1T) | semiconductor (2H) phase transition of dispersed 2D MoS_2 crystalline phase in graphene matrix.

(3) Providing detailed experimental data and a solid scientific basis for the successfully synthesizing layered materials include 2D MoS_2, graphene oxide and MoS_2/C NC by hydrothermal approach and, establishing a method with suitable experimental parameters to fabricate MoS_2/C NC with structures such as "sandwich", "layer-by-layer", "vertical-stacked" and "anchored".

(4) Initially building a scientific basis for a larger-scale manufacturing method of atomically thin 2D MoS_2, graphene oxide and graphene-based functional materials with high applicability in the fields of supercapacitor, energy storage, photovoltaics and optical applications.

Futural prospective extended research

(1) Research on fabrication and applications of Moiré pattern heterostructures of the MoS_2/graphene nanocomposite with non-linear optical properties such as strong four-wave mixing (FWM), sum-frequency generation (SFG), and second-harmonic generation (SHG).

(2) Investigating the memristive property of the MoS_2/C NC for memristor applications.

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