

Formation of Hierarchical 2D-MoS₂ Nanostructures over Carbon Fabric as Binder Free Electrode Material for Supercapacitor Applications

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Abstract

Carbon fabrics are the new generation promising electrode materials for super capacitors owing to their high electrical conductivity, high chemical stability and low thermal expansion. In this work, 2D-MoS₂ nanostructures have been successfully deposited over the commercially available carbon fabric by hydrothermal approach, using silicotungstic acid as an additive. MoS₂ nanostructures – carbon fabric was broadly characterized using XRD, FESEM and Raman Spectroscopy. XRD patterns indicated that the fabricated MoS₂ nanoparticles can be indexed to hexagonal (2H) and rhombohedral (3R) phases. FESEM images revealed the formation of hierarchical 2D MoS₂ nanosheets arranged in a nanosphere like morphology over the carbon fabric. The electrochemical behavior of the MoS₂ - carbon fabric and commercially available bare carbon fabric were studied using cyclic voltammetry analysis with different scan rates. The MoS₂-carbon fabric exhibited an excellent electrochemical performance with a specific capacitance of 441 F/g at a scan rate of 10mV/s. The good cyclic behavior with symmetric charging/discharging curves, constant specific capacitance for longer scan rates, suggesting that the MoS₂- carbon fabric electrode is a potential electrode material for high power applications.

Keywords: Carbon Fabrics (CF); 2D materials; MoS₂ Nanosheets; binder-free electrode; Supercapacitors;

Introduction

Supercapacitors, also known as electrochemical capacitors, have been acknowledged for over fifty years and considered as one of the potential energy storage systems in addition to batteries, for various diverse applications such as portable electronics, surge power delivery devices for electric vehicles and digital calipers [1]. In recent years, tremendous efforts have been made to develop the electrode materials for supercapacitor applications to meet the energy requirements of daily life. The electrode materials for supercapacitor falls under three categories namely electrical double layer capacitors (EDLC), pseudocapacitors and hybrid capacitors [2-7]. In EDLC, the electrical energy can be stored based on the following phenomena of either charge accumulation at the electrode and electrolyte interface, e.g., carbon-based materials and graphene, which has high surface area, excellent electrical conductivity. In pseudocapacitors, the energy can be stored by reversible faradic redox reactions, e.g., transition metal oxides/hydroxides and conducting polymers, which has high specific capacitance and energy density. The hybrid capacitors are the combination of EDLC and pseudocapacitors.

Scientific community people are focusing on fabricating the high-performance supercapacitor with excellent electrochemical performance, flexible, binder free to their potential applications in flexible energy storage devices. To achieve the high-performance supercapacitors, hybrid electrode materials are highly recommended because of having excellent electrical conductivity, high surface area and high theoretical capacitance values. Recently, two-dimensional (2D) materials like transition metal dichalcogenide (TMD) such

as MoS₂, WS₂, and SnS₂ have gained attraction because of their unique electrical, optical and mechanical properties [8].

Among these, 2D-TMD materials MoS₂ has attained special attention because of its earth abundant, large surface area and 2D structure preferring ion adsorption and transports but limited by its low intrinsic conductivity which leads to low energy density [9,10]. Additionally, while preparing the MoS₂ based electrode materials, utilizing the binders and conductive agents decreases the energy density [11]. By considering the above facts, binder free fabrication of MoS₂ nanostructures over the conductive substrates are quite appealing to develop the supercapacitors with excellent electrochemical performance. Because of inimitable properties like high flexibility, low cost, excellent electrical conductivity, good physical strength, carbon fabric (CF) is highly recommended to fabricate the binder-free electrodes for supercapacitor applications [12].

In this work, we report the simple hydrothermal synthesis of agglomerated 2D MoS₂ nanosheets arranged over the commercially available CF, like 2D MoS₂ nanospheres morphology. The electrochemical performances of the fabricated MoS₂ – CF was further investigated using electrochemical measurement system. It was found that the supercapacitor constructed with this type of binder-free electrode material exhibited a specific capacitance of 441 F/g at the scan rate of 10mV/s, which offers a new generation two-dimensional electrode material for supercapacitors. For comparison, the electrochemical investigation of commercially available CF was also performed to check the influence of 2D MoS₂ for the supercapacitor applications.

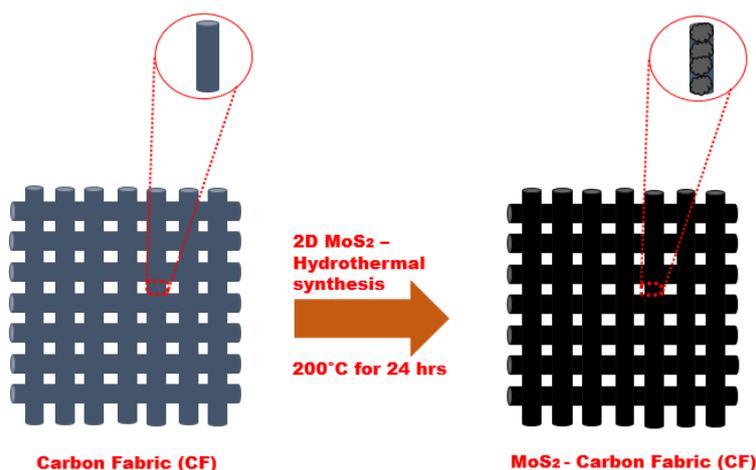


Fig.1. Schematic representation- Fabrication of MoS₂ nanostructures over CF, using hydrothermal synthesis.

Materials and Methods

All chemicals used were of analytical grade, purchased from Wako chemicals, Japan. Carbon fabric (CF) was purchased from sainergy fuel cell India, pvt limited. The commercially available bare CF and the fabricated binder free 2D-MoS₂-CF electrodes were studied using X-ray diffractometer, XRD (RINT-2200, CuK α radiation, Rigaku) with 0.04 °sec⁻¹ scan rate in the 2 θ range from 20° to 80°, Raman scattering spectroscopy (NRS-7100, JASCO) with a laser excitation wavelength of 532 nm (spot size 1 μ m) and field-emission scanning electron microscopy, FE-SEM (JSM 6335F, JEOL). Electrochemical characterizations were performed using CHI 600 series standard three electrode electrochemical Analyzer/Workstation. Here, the MoS₂ – CF as working electrode, Ag/AgCl (saturated KCl) as reference electrode and platinum wire as counter electrode were used along with 0.5M of Con.H₂SO₄ as an electrolyte, during the electrochemical analysis. Electrochemical impedance spectroscopy (EIS) analysis were also carried out from 100 kHz (Higher frequency) to 0.1 Hz (lower frequency) at open circuit potential with an AC perturbation voltage of about 5 mV.

Figure 1 shows the schematic representation of fabrication of MoS₂ nanostructures over CF, using hydrothermal synthesis. Prior to synthesis, commercially available CF was treated in ultrasonic bath with

ethanol for about 1 hour, and then washed with distilled water to remove the impurities, which was used as a conductive template for the growth of MoS₂ nanostructures. 0.5 g of Na₂MoO₄ · 2H₂O and 0.7g of CH₃CSNH₂ were dissolved in 50ml of distilled water. Then, 8.0g of silicotungstic acid was added into the reaction mixture solution under vigorous stirring. The mixture solution along with the CF was then transferred into a 100 mL Teflon-lined stainless-steel autoclave apparatus and kept at 200 °C for 24 hrs. After cooling to room temperature, the fabricated binder free MoS₂ – CF electrode was taken from the autoclave and washed with absolute ethanol and distilled water for several times and annealing at 300 °C for 5 hrs.

The capacitance values were calculated from CV data according to the following equation,

$$C_{device} = \frac{1}{v(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \dots\dots\dots \text{(Equation 1)}$$

where v is the scan rate, V_f and V_i are integrated potential limits of voltammetric curve and I(V) is the voltammetric discharge current. Specific capacitance of the electrodes can be calculated by the relation,

$$C = \frac{C_{device}}{m} \dots\dots\dots \text{(Equation 2)}$$

Where, m is the mass of the electrode material, respectively.

Results and Discussion

For the growth mechanism [13], it is clearly characterized that the chemical reaction of sodium molybdate with silicotungstic acid tends to form molydosilic acid (from equation 3) under acid condition whose typical form is H₄SiMo₁₂O₄₀. On the other hand, the Mo (VI) can be easily reduced with some reductants such as H₂S in the solution [14,15]. During the hydrothermal process, the reductant is H₂S which was provided by CS(NH₂)₂, (from equation 4) because CS(NH₂)₂ can be easily decomposed in solution [16]. Thus, the oxidation–reduction reactions held during the hydrothermal process should be responsible for the formation of agglomerated MoS₂ nanosheets in to MoS₂ nanospheres like morphology over the CF (from equation 5). The intermediate product H₄SiMo₁₂O₄₀ could serve as a self-sacrificial template for the subsequent growth of MoS₂ nanospheres like morphology. Based on the above analysis, the reaction mechanism for the formation of MoS₂ nanostructures can be expressed as follows:

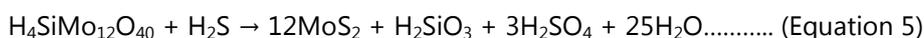
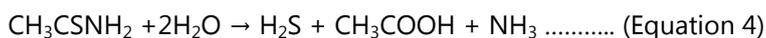
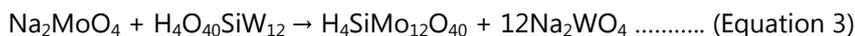


Figure 2 represents the XRD analysis of (a) commercially available CF and (b) the fabricated MoS₂ - CF. The diffraction crystal planes (002) and (100), corresponded to the hexagonal primitive structure of carbon (JCPDS 89-8487) [17]. The diffraction peaks correspond to (002), (100), (101), (103), and (105) reflections, signified the nanostructured 2H-MoS₂ (JCPDS 37-1492) [18]. And the diffraction peaks which correspond to (004), (101) indicated the nanostructured 3R-MoS₂ (JCPDS 17-0744) [19].

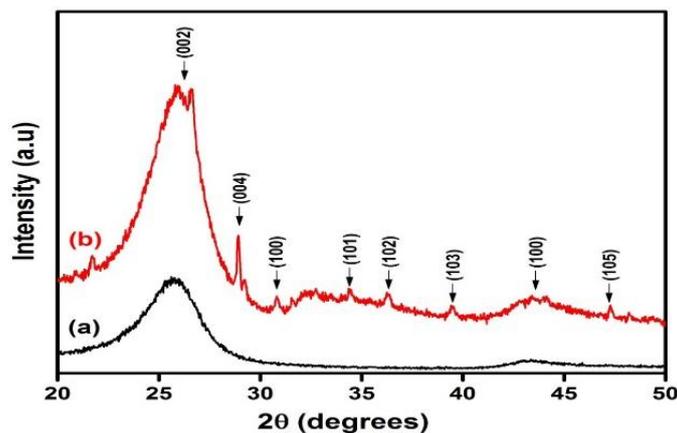


Fig. 2. XRD Analysis of (a) CF and (b) MoS₂ - CF.

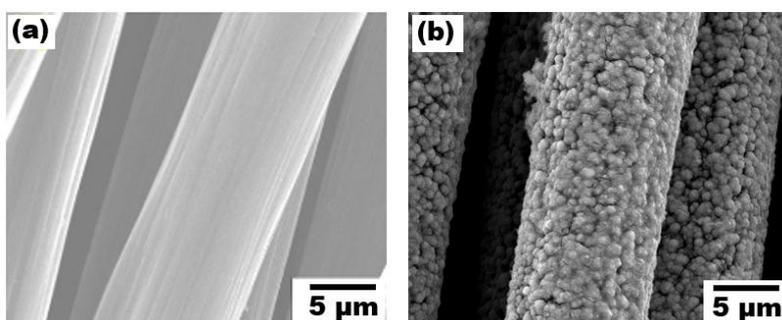


Fig.3. FESEM analysis of (a) CF and (b) MoS₂-CF.

Figure 3 shows the typical FESEM analysis of (a) CF and (b) MoS₂– CF. From Figure 3(a), it is clearly seen that the carbon fabrics are compactly packed with random orientation in order to form a macroporous open structure [20,21]. This kind of porous material provide better accessibility to the electrolyte. Hierarchical 2D MoS₂ nanosheets were agglomerated in to MoS₂ nanosphere like morphology with uniform distribution over the CF, as shown in Figure 3(b). Thus, this type of 2D- MoS₂ nanostructures over the CF facilitates an excellent electrochemical performance for high power applications, because of its high surface area.

Figure 4 shows the Raman spectroscopy (a) CF and (b) MoS₂-CF. From the Raman spectra of Figure 4(a) and 4(b), the two high intensity peaks obtained at 1349 cm⁻¹ and 1586 cm⁻¹, depicted the D and G bands of CF [22]. Hence, the calculated I_D/I_G ratio for MoS₂ – CF and CF are 1.2 and 1.14 respectively. From Figure 4(b), the obtained Raman modes (in-plane optical vibration of Mo and S atoms) E¹_{2g} (403 cm⁻¹) and E²_{2g} (377 cm⁻¹), with the frequency difference of 26 cm⁻¹, represented the five-layer formation [23].

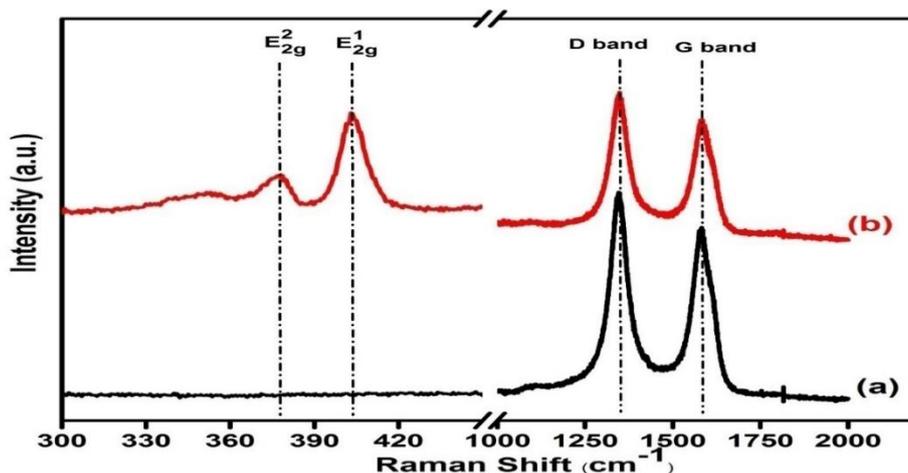


Fig. 4. Raman spectroscopy analysis of (a) CF and (b) MoS₂-CF.

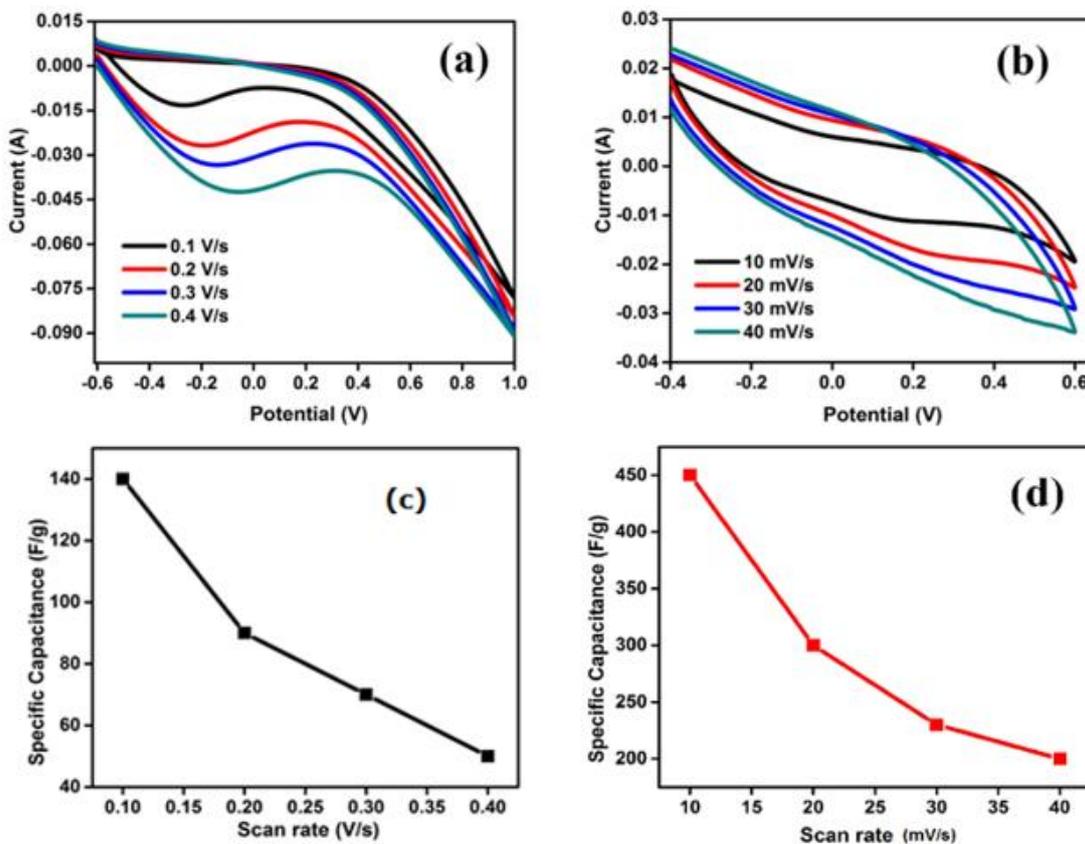


Fig. 5. Cyclic Voltammetry (CV) analysis of (a) CF and (b) MoS₂-CF. Relation between Specific capacitance and Scan rate.

The cyclic voltammetry (CV) analysis of CF and MoS₂-CF were shown in Figure 5(a) and (b). The CV analysis of CF exhibited an exceptional performance with asymmetric curve pattern of charging/discharging electrochemical behavior of specific capacitance value as 145F/g at the scan rate of 0.1V/s, as shown in Figure 5(a). From Figure 5(b), it is clearly seen that the fabricated binder free MoS₂-CF exhibited an enhanced electrochemical performance with almost rectangular pattern of cyclic loop with maximum specific capacitance value as 441 F/g at the scan rate of 10mV/s. The enhancement in capacitance is due to the increased surface area of MoS₂-CF. This behavior of symmetric in charging and discharging cycles helps to use it in high power applications. This linear and symmetric curve exposed the good capacitive electrochemical behavior of MoS₂-CF. Variations of specific capacitance for different scan rates were represented in Figure 5(c) and (d). It revealed that constant value of specific capacitance can be achieved at higher scan rates, which is the potential significance of the electrode materials.

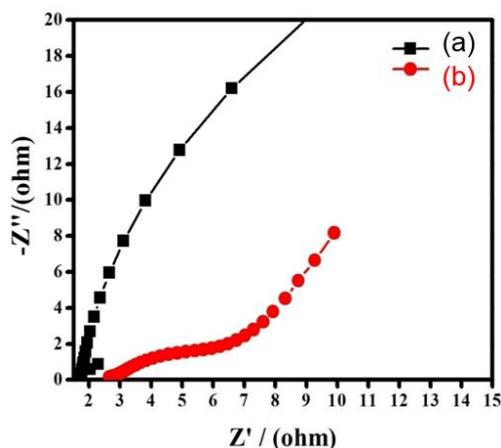


Fig.6. Electrochemical impedance Spectroscopy(EIS) analysis (a) CF and (b) MoS₂– CF.

Figure 6 represents the electrochemical impedance spectra(EIS) of CF and MoS₂– CF. Figure 6(a) depicts the impedance spectra of CF. From Figure 6(b), the impedance plot of MoS₂-CF shows a quadrant circle in the higher frequency region and a 45° capacitive slope in the lower frequency region. The higher frequency intercept of the quadrant circle on the real axis of the impedance plot is the combination of the resistance of the electrolyte, the intrinsic resistance of the active material of MoS₂-CF and the contact resistance between the active material MoS₂ and the current collector CF.

Conclusions

Formation of hierarchical 2D MoS₂ nanostructures over the carbon fabric (CF) was demonstrated using a simple hydrothermal route. FE-SEM analysis exposed the formation of MoS₂ nanospheres like morphology over the CF with homogeneity. FE-SEM results are in good agreement with XRD and Raman results. Electrochemical analysis revealed the excellent electrochemical performance of MoS₂ - CF electrode with the specific capacitance value of 441 F/g at a scan rate of 10mV/s, suggesting that it is a potential electrode material for high power applications.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

This work was financially supported in part by a JST CREST Grant Number JPMJCR15Q7, Japan.

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