Growth of 3-Dimentional MoS₂-PANI nanofiber for high electrochemical performance

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Abstract

The preparation of few layered 3D material Molybdenum/Polyaniline (MoS₂/PANI) nanofiber (NF) composite synthesis via a hydrothermal process. MoS₂/PANI nanofiber composite was characterized via Fourier-transform infrared (FT-IR) spectra to study the chemical functional group and their interaction, and optical properties examine by the UV-visible spectra. Formation of nanosheet and 3D hierarchical flower morphology was examined through Field emission scanning electron microscopy (FESEM), and the elemental analysis examined through Energy-dispersive x-ray (EDX), and Transmission electron microscopy (TEM). XRD studies show the properties of crystalline nature of the nanocomposite. Binding energy and composite elemental identified states measured through x-ray photon spectroscopy (X-PS). The Electrochemical technique was used to investigate cyclic voltammetry, and electrochemical catalytic activity evaluated from EIS which obtained resistance is 137.52 Ω, 66.40 Ω, and 15.25 Ω respectively. Linear sweep voltammetry, CV oxidation peak reached maximum oxidation current is 2.72 × 10⁻⁴ Amperes, and curve appeared between −4.5 to 4.5 Volt. Finally MoS₂-PANI-1 Nanofiber composite is prominent material for electrochemical performance.

1. Introduction

Recently, conducting polyaniline nano composites have paid an important role in the sensors and energy storage devices [1]. Conducting polymers (CPs), like polypyrrole (PPy), polyaniline (PANI), polythiophene (Pth), and poly (3, 4-ethylenedioxythiophene) are having high electrical conductivity, and power density maybe deserved to use in sensors, and electrochemical devices [2–5]. Among all, PANI is exhibits high electrical conductivity because polymer contains conjugate alternatively double and single bond or π-electron in their backbone may able to showing the metallic or semiconducting properties, so it is called ‘synthetic metal’ Alan MacDiarmid’s et al reported [6]. If polymer associated with nanocomposite enhanced its large surface area and power density may in favors of electrochemical properties, high specific capacitance, and good environmental stability. Various one-dimensional materials were observed different morphology nanorods, nanotube, and nanofibers which offers several potential applications in various fields such as electrochemical sensors, [7] super capacitors, solar cell, and solid state batteries.

Currently, highly active electrocatalyst materials are graphene quantum dots, multi walled carbon nanotubes, di-nickel phosphide, and molybdenum disulphide shows as a promising catalytic performance investigated in the hydrogen evolution reaction [8, 9]. In recent years hierarchical nanostructure has become a hot topic due to electrochemical behavior of electrode materials are significantly dependent on their morphology, size and structure MoS₂ nanosheets are layered transition metal dichalcogenide constructed S-MoS three layers atoms arranged by weak Vander Waals forces, in which covalent bond strongly attached to Mo and S atoms, and variable oxidation state [10]. MoS₂ have attracted significant attention in the area of electrochemistry and biochemistry, MoS₂ which as anode transition metal sulphide material, this material intrinsically less ion conductivity exhibit, when doped with conductive polymer increases the conductivity.
because of polymer matrix contain π-electron in their backbone [11, 12]. 2-Dimensional MoS2 hybrid nanocomposite highly influences the optoelectronic properties due to 1.8 eV direct bandgap, MoS2 are potential catalysts for photochemical hydrogen evolution [13], microelectronics, and sensors [14]. Synthesis of MoS2 nanocomposite by hydrothermal process, the main advantage of this method gives a high surface area and raises the crystallinity nature in 2D materials; Hu et al [15] have been assembled 3D hierarchical MoS2/PANI and MoS2/C for lithium ion battery. In view of electrochemical characteristics, the electrode materials highly related to their surface morphology, Chao et al [16] fabricated the hierarchical MoS2/PANI nanosheets array vertically aligned on the rGO nanosheets were prepared through chemical route and hydrothermal method, PANI matrix is intercalated with MoS2 nanosheets electrochemical performance reveals that excellent cyclic stability and high specific capacitance.

In this study compared with the available literature, the synthesized PANI NF and MoS2/PANI hybrid composites In-situ chemical oxidation and hydrothermal techniques, the morphology structure of PANI NF reveals the fibrous structure have a good diameter and high surface area. 3D MoS2/PANI nanofiber composites which have dominated the large specific area, high electrical conductivity, good mechanical strength, and unique morphology. MoS2 nanosheets are embedded on PANI NF, MoS2 which has layered structure possess the nanostructure morphology and crystalline nature, conventionally the crystallinity nature improves an electrochemical mechanism. CV curve shows the rectangular shape which enhances the excellent surface area for various sweep rate, EIS Nyquist plot indicates the small Rct resistance value 66.40 Ω and 15.25 Ω shows the fast electron transfer and hybrid nanocomposites increases the electron diffusion. These are evidence for the promising electrochemical performance.

2. Materials and methodology

Aniline (99.5%) Purchased from Sigma-Aldrich, Ammonium molybdate tetrahydrate (AMTH), Ammonium peroxydisulfate (APS) and Thiourea Purchased from Merck India. All reagents are analytical grade used without purification. The Aqueous solution was prepared by using pure double deionized water (DDW).

2.1. MoS2 - PANI NF synthesis

1.3 g (NH4)2MoO4·4H2O and 3.34 g of aniline were dissolved in 40 ml of water, and then 1M HCl added dropwise adjust pH 4–5. The stirring at 50 °C about 2 h resultant product of MoO2(C6H8N2)2·2H2O were collected and dried at 50 °C [17]. Then 0.34 g of MoO3(C6H8N2)2·2H2O and 0.5 g of (NH4)2MoO4·4H2O and 0.57 g of (NH4)2S2O8 were dissolved in 40 ml of water subsequently adjust pH 2 using 1M HCl with continuous stirring about 6 h, the further mixture was centrifuged and dried at 50 °C 12 h. Collected MoOx/PANI nanofiber were assembled through Hydrothermal process MoOx/PANI nanofiber sample 0.4 g and 0.3 g of thiourea dispersed in 20 ml of deionized water, the solution was transferred to a 50 ml of Teflon containing stainless-steel autoclave and treated at 200 °C for 48 h final obtained MoS2/PANI nanofiber was collected by centrifugation and washed with distilled water several times finally dried at 50 °C overnight. number 2 sample synthesized similar process, but in the second step change the concentration of AMTH 10.114 mM to 25 mM.

2.2. Synthesis of polyaniline nanofiber

Polyaniline nanofiber prepared via chemical polymerization, 0.3 ml of aniline, and 10 mm Camphor sulphonic acid (CSA) dissolved in 10 ml of 1M Hydrochloric acid (HCl) and 0.18 g Ammonium peroxydisulfate (APS) dissolved in 10 ml of 1M HCl. The aqueous solution APS were added dropwise over the organic solution of aniline with constant stirring, then dark green layer formed kept 6 h undisturbed obtained product washed with distilled water several times finally obtained product dried at 60 °C 24 h as shown in the scheme 1.

2.3. Material characterization techniques

The synthesized PANI NF, MoS2/PANI-1, and MoS2/PANI-2 nanocomposite surface morphology and EDX was studied by Field emission-Scanning electron microscopy (FE-SEM). UV-Visible spectra were measured through Perkin Elmer Lambda 350 UV-Visible Spectrometer. Fourier-transform infrared (FTIR) spectra were investigated by Bruker Alpha ATR-FTIR. The chemical oxidation state and elemental identification analyzed via x-ray Photoelectron Spectroscopy using Kartos Axis Ultra DLD. Electrochemical characterization performed using the CHI660E electrochemical Workstation.
3. Results and discussion

3.1. Scanning electron microscopy

The morphology images of MoS$_2$/PANI-1, MoS$_2$/PANI-2, and PANI NF samples were characterized by FE-SEM as shown in the figures 1(a)–(d). MoS$_2$/PANI-1 and MoS$_2$/PANI-2 nanocomposite show a glomerulus nanofiber covered with edge rich MoS$_2$ multi nanosheets structure has appeared on the surface of PANI NF.

MoS$_2$/PANI-1 shows the glomerulus like nanofiber with 3 dimensions fused flower multi shaped edge cited in figures 1(a)–(b) [18, 19] and MoS$_2$/PANI-2 the size is reduced confirmed the molybdenum layers embedded on PANI NF is as shown in figures 1(c)–(d). Figure 1(e) PANI NF shows the fibrous morphology structure depends on dopant acid and concentration of Aniline and APS, nanofiber prepared via in situ chemical method with mechanical agitation 4 h and kept 12 h, which is enhance the surface area and stability of the material. However, 1D PANI nanofiber incorporates with 2D MoS$_2$ has established dramatically formation of 3D PANI/MoS$_2$ Nanofiber evidenced from morphology.

3.2. EDX elemental analysis spectra

In figures 2(a)–(b) The EDX elemental analysis of MoS$_2$/PANI-1 and MoS$_2$/PANI-2 nanofiber composite reveals the presence of carbon, nitrogen, oxygen, molybdenum, and Sulphur. The weight percentage of C, N, O, Mo and S sample refers to the 8.16%, 9.85%, 10.74%, 41.14% and 30.06 and 8.98%, 9.91%, 10.94%, 37.82% and 29.94% respectively [20]. These elemental analyses of composite indicate specific chemical elements are presented in the composite. The elemental composition was examined through EDX to determine the chemical composition of elements.

3.3. HR-transmission electron microscopy

The TEM images of PANI NF is shows the fibrous structure is as shown in figure 3(a).

Figure 3(b) MoS$_2$/PANI-1 composite TEM images which show that the MoS$_2$ layer embedded on PANI NF. The dark region is the PANI and the lighter region is the MoS$_2$ [21, 22]. The entire structure reveals superior catalytic properties, and electrochemical efficiency.

3.4. Fourier-transform infrared (FT-IR) analysis

FTIR spectra recorded in the range 500 to 4000 cm$^{-1}$ to investigate the chemical composition, and formation of bonds in MoS$_2$/PANI-1, MoS$_2$/PANI-2 composite, and PANI NF is shown in figure 4. Pure PANI NF the band at 1682, 1512, 1288 and 1098 cm$^{-1}$ are respectively. The MoS$_2$/PANI-1 composite band observed at 1684 & 1512 cm$^{-1}$ are assigned with the C=C stretching vibration mode of the Quinonoid (Q) and Benzenoid (B) unit respectively [15]. The peak at 1354 cm$^{-1}$ and 1134 cm$^{-1}$ are associated with C–H in Q and B units. MoS$_2$/PANI-2 peaks moved towards right the intensity increases.

The peak indicates the Mo–O stretching and vibration of O–H observed bands at 1692 and 1152 cm$^{-1}$ respectively [20]. Peaks at 909 cm$^{-1}$ and 588 cm$^{-1}$ were located to the S–S and Mo–S, MoS$_2$/PANI Composite [23].

3.5. UV-visible spectroscopy

To study the UV-Visible absorption spectra intercalation of PANI NF, MoS$_2$/PANI-1 and MoS$_2}$/PANI-2 Nanofiber composite. Figure 5(a) is the pure PANI NF absorption spectra shows peak at 244, 356 and 632 nm.
The absorption peaks are present in the UV and visible region spectra assigned due to $\pi - \pi^*$ transition and these indicate the C=C, benzenoid and quinonoid unit \cite{24,25}. Figure 5(b) the MoS$_2$/PANI-1 composite peak shows the 303 nm, 609 nm and MoS$_2$/PANI-2 composite 239 and 580 nm corresponding to polaron-$\pi^*$ transition, obviously this peak appearing in the redshift due to presence of MoS$_2$. Absorption and wavelength peak highly dependent on the number of MoS$_2$ layers. In MoS$_2$/PANI-1 and 2 composite has many layers due to the direct electron band gap material. \cite{6} The hybrid composition enhances the absorption intensity and free charge carriers. Indicates the well distribution of PANI in the MoS$_2$-PANI composition.

3.6. XRD analysis

The crystal structure of MoS$_2$/PANI nanofiber and PANI NF measured by XRD. In figure 5. The distinctive peak located at 2 theta at 13.82°, 33.10°, and 58.68° corresponding crystal planes of (002), (100), and (110) respectively. \cite{16,22} The additional broad diffraction peak assigned at 24.76° indexed plane (200), confirms the presence of PANI in the MoS$_2$ nanocomposite. \cite{6} This suggests a hydrothermally prepared nanocomposite strongly influenced the high crystallinity properties in the material. It can be clearly seen that the hexagonal structure of MoS$_2$.

Figure 1. FE SEM images of (a)–(b) MoS$_2$/PANI-1 (c)–(d) MoS$_2$/PANI-2 different magnification resolution and (e) PANI nanofiber.
3.7. X-ray photon spectroscopy (XPS)

XPS was measured to identify the composite elemental of molybdenum (Mo), Sulphur (S) in the MoS2/PANI material as shown in figure 6. Mo 3d spectrum, shows the two broad peaks locating binding energy at 228.6 eV, and 231.8 eV are corresponding to Mo 3d 5/2 and Mo 3d 3/2 S 2s respectively. The S 2s peak located around 225.9 eV, as shown in figure 6(a).

Furthermore, S 2p spectrum peaks at 161.56 eV and 162.77 eV are assigned S 2p 3/2 and S 2p 1/2, as shown in figure 7(b). These XPS spectra data values confirms the homogeneous distribution of PANI on MoS2 material both are well intercalation, and successfully formation of MoS2/PANI composite.

3.8. Electrochemical performance

The electrochemical measurements were carried through the CHI660E electrochemical workstation using three electrode systems using Platinum wire as a counter electrode, Ag/AgCl Reference electrode, and Stainless steel substrate with MoS2/PANI as a working electrode. To fabricate the working electrodes, prepared samples, Activated charcoal, and Polyvinylidene fluoride (PVDF) with ratio (80:10:10 w/w) were dissolved with N-Methyl-2-Pyrrolidone (NMP) to form a slurry. The slurry was coated on a stainless steel substrate and dried at 60 °C 8 h.

In figures 8(a)–(b) shows the CV study for MoS2/PANI-1 and MoS2/PANI-2 Nanofiber CV curves at various scan rate from 0.1 V s⁻¹ to 0.5 V s⁻¹ while varying the scan rate oxidation peak and reduction peak gradually shifts towards the positive and negative potential [17]. This CV curve shows the rectangular structure,
which exhibits a large surface area, high conductivity, and electrochemical cyclic stability [26]. Where MoS$_2$/PANI-1 anodic peak current $I_{p,a}$ maximum current shows the $2.72 \times 10^{-4}$ A, MoS$_2$/PANI-1 Nanofiber exhibit high electrochemical performances [6].

3.9. Electrochemical impedance spectra
To determine the electrochemical behaviour for PANI, MoS$_2$/PANI-1, and MoS$_2$/PANI-2 Nanofiber composite is in figure 9. The obtained Nyquist plot shows are perfect quasi semicircle from low frequency zone to high frequency zone for a different composition. PANI nanofiber obtained charge transfer resistance is 137.52 $\Omega$, then hybrid heterostructure composition enhances the properties of electron transfer resistance of MoS$_2$/PANI-1 and MoS$_2$/PANI-2, 66.40 $\Omega$ and 15.25 $\Omega$ respectively as shown in figure 9 [27]. When enhances the charge transfer process for different composite the curve simultaneously decreases the resistance values, small $R_{ct}$ resistance value enhances the charge transfer diffusion process, MoS$_2$/PANI-1, and MoS$_2$/PANI-2 nanofiber composite efficient for electrochemical properties.

4. Linear sweep voltammetry
LSV examine the different scan rate were conducted on the MoS$_2$/PANI-1 and MoS$_2$/PANI-2 Nanofiber composite as shown in figures 10(a)–(b).
Figure 6. XRD patterns of PANI NF, and MoS$_2$/PANI-1 composite.

Figure 7. The XPS spectra of (a) Mo 3d and (b) S 2p for MoS$_2$/PANI composite.

Figure 8. CV plots for (a) MoS$_2$/PANI-1 (b) MoS$_2$/PANI-2 NF composite different scan rate.
MoS$_2$/PANI fiber composite LSV graph shows the while varying the sweep rate from 0.1 V to 0.3 V, oxidation current increases simultaneously, here electron diffusion ions and charge transfer process enhance the stability of the material, MoS$_2$/PANI-1 composite I-V characteristic curve linearly shows the more stability than MoS$_2$/PANI-2 composite, this composite enhances the superior I-V characteristics the applied voltage range $-2$ to $+2$ V [28].

4.1. Conclusions
In this present work successfully synthesized the PANI fiber and MoS$_2$/PANI fiber composite by chemical In-situ and hydrothermal method. MoS$_2$/PANI nanofiber composite clearly shows the formation of multilayers embedded on PANI NF morphology. CV peak increased maximum oxidation current is $2.72 \times 10^{-4}$ A and high surface area, electrochemical catalytic activity exhibit good, MoS$_2$/PANI nanofiber composite confirms the elemental analysis and superior electrochemical properties.

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