Ordered mesoporous carbon provoked dimensionally varied molybdenum dichalcogenide: A striking sensing matrix for electrochemical detection of hydrazine

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Abstract

Rational design and construction of two-dimensional transition metal dichalcogenides (TMDs) with minimal size are vital for improving the sensitivity and selectivity of the electrochemical sensors. Here we demonstrated a vast surface triggered size reduced MoS₂ formation on ordered mesoporous carbon (OMC) support. The OMC support material was synthesized through hard templating approach using mesoporous silica SBA-15. Subsequently, the MoS₂-OMC nanocomposite material was obtained through hydrothermal route. The structural properties of the prepared materials prove the existence of a well-defined mesoporous nature of carbon and flower-like MoS₂ on the surface of OMC. The developed MoS₂-OMC composite was deployed as a sensing matrix for the detection of hydrazine in neutral medium. The electrochemical results illustrated that the prepared composite materials exhibited excellent activity towards hydrazine detection with a wide linear detection range (1–9 μM) and very low detection limit of 0.4 μM with a sensitivity of 0.25 μA/μM respectively.

Keywords MoS₂ · Mesoporous carbon · Composite structure · Hydrazine sensor

1 Introduction

Hydrazine is an essential chemical that has been widely used in various applications like antioxidants, emulsifiers, and rocket propellants. However, its exposure to the human system affects them in many ways [1, 2]. Due to hazardous nature, it is very essential to develop a detection protocol for a selective and sensitive determination of hydrazine. So far numerous methods such as fluorescent assay [3], titrimetry [4], potentiometry [5], chromatography [6], flow injection analysis [7] and electrochemical technique have been utilized for the determination of hydrazine. Among all, the electrochemical technique is the best method because of its high sensitivity, fast response, affordability, and real-time utility [8–11]. However, the

electrochemical hydrazine oxidation at unmodified electrodes is restricted due to sluggish kinetics and requires very high overpotential, which ends up with a poor sensing performance [12]. To overcome this, a strategy of utilizing single or composite electroactive nanomaterials with enhanced sensitivity and selectivity was proposed [13, 14]. Numerous composite materials were tested for detecting a vast spectrum of biomolecules; it includes the most studied glucose [15, 16] and hydrogen peroxide [17, 18]. In the recent scenario, the unique two-dimensional transition metal dichalcogenides (TMDs) such as MoS₂, WS₂, and MoSe₂, etc., have been attracted much attention in a huge number of applications including electronics [19, 20] electrocatalysis [21, 22] electrochemical sensors [23, 24] and electrochemical energy-related applications [25,

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26]. Within the group, the layered MoS_2 structure attracted much interest in electrochemical applications. With the existence of a wide tunable bandgap nature of materials, it shows excellent electronic properties [27, 28]. Altering the bandgap by doping with foreign metals leads to significant physicochemical properties [29, 30]. Meanwhile, reducing the size in a single layer or by quantum size, important properties like photoluminescence were observed [31, 32]. Recently these MoS_2 layered structures have highly emerged in the field of electrochemical sensors for the detection of the bioanalytes [33, 34]. The available literature pointed out that though these materials show excellent electrochemical activity, miniaturization into individual slap leads to enhanced activity. Therefore, different synthetic routes are attempted for the development of single slap MoS_2 [35]. Further, the fabrication of electrochemical devices for sensor and catalysis applications using homogenized single-layer MoS_2 is still a challenging task. As such, in our previous work, we demonstrated that the hydrothermal growth of MoS_2 on the silica support shows significant advantages than the unsupported one [36]. In this present work, further scale-up of MoS_2 for electrochemical application is attempted and the unique MoS_2 -OMC composite electrode is fabricated for electrochemical sensing applications. The prepared composite materials showed well structural characteristics and the electrochemical sensor activity was verified with hydrazine.

2 Materials and methods

2.1 Chemicals and materials

The analytical reagent (AR) grade chemicals were purchased by global suppliers such as Merck and Sigma-Aldrich. All the chemicals were used as received without further purification. Meanwhile, the solutions which are utilized for electrochemical sensing studies were prepared using milli-Q (18.2 M Ω cm) water.

2.2 Synthesis of mesoporous silica (SBA-15) and mesoporous carbon (OMC)

The micellar mechanism was adopted for the synthesis of SBA-15 material. Here, the Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) co-polymer, [Aldrich, Mw = 5800] and tetraethyl orthosilicate (TEOS) were used as a structure-directing agent and silica source respectively. In a typical synthesis, 3 g of Pluronic P123 was dispersed in a calculated amount of distilled water, and the resultant solution is mixed with 2 M HCl at 40 °C. Then 6.3 g of TEOS was added to the above resultant solution. The mixture was stirred at 40 °C

for 24 h and then aged at 100 °C for 48 h without stirring. The obtained solid product was recovered by filtration, washed with deionized water and dried at 80 °C overnight. Calcination was carried out in static air at 550 °C for 8 h. [37]. Meanwhile, the OMC materials were prepared by a hard-templating approach by utilizing mesoporous silica SBA-15 as a hard template. In detail, a calculated amount of sucrose, sulfuric acid, and water were mixed with 1 g of mesoporous silica and the mixture was stirred for 12 h at room temperature. This mixture was dried at 100 °C for 6 h, after that the oven temperature was increased to 160 °C and kept it for another 6 h. Similar steps were repeated to completely cover the mesoporous silica surface by carbon precursors. Finally, the as-synthesized silica-carbon composite was carbonized at 900 °C for 4 h at the inert gas atmosphere and the silica template was removed using hot NaOH solution.

2.3 Synthesis of MoS_2 -OMC composite

The hydrothermal synthesis was adopted for the MoS_2 -OMC composite formation. In a typical synthesis, 0.15 g of sodium molybdate, 0.18 g of thiourea and 0.016 g of polyethylene glycol were dissolved in a calculated quantity of deionized water. The entire mixture was stirred for 2 h and then 0.4 g of OMC support was added to the above mixture and further stirred for 12 h. The final mixture was transferred into a Teflon lined autoclave and hydrothermally heated at 180 °C for 24 h. The as-synthesized product of MoS_2 -OMC was washed and dried at 80 °C for 12 h.

2.4 Characterization

The structure and phase formation of OMC, MoS_2 , MoS_2 -OMC composite material was characterized by an X-ray diffractometer (Bede Scientific Ltd., UK; CuK α radiation; operated at 40 kV, 45 mA; λ = 0.15418 nm). In XRD analysis, the diffraction angle was measured ranging from 10 to 80 2 θ value. The vibrational characteristics of the synthesized samples were verified using Renishaw Invia Raman Microscopy. He-Ne laser source of 632.8 nm wavelength and 18 mW intensity was utilized to measure the Raman features of the samples. Morphological features of MoS_2 and composite materials were characterized by (FESEM, ZEEIS X-Max Oxford Instruments) and TEM using Tecnai G20, operating at 200 kV. The oxidation state and composition were examined using X-ray photoelectron spectroscopy (XPS). The Multilab 2000 Thermo scientific (UK) X-ray photoelectron spectrometer with Mg K α X-ray (1253.6 eV) and 200 W power was used as the exciting source and 10 eV energy pass was used for data collection.

2.5 Electrochemical sensor activity studies

The Potentiostat/Galvanostat BAS 100B (Bioanalytical Systems Inc.) was utilized for the electrochemical experiment. All the electrochemical sensing experiments were carried out at an ambient temperature ($25 \pm 1^\circ\text{C}$) using a three-electrode system. In detail, a glassy carbon electrode (GCE) modified with the catalyst ink served as working electrode. The standard Ag/AgCl (3 M KCl) and Pt wire served as reference and counter electrodes respectively. The catalyst ink was prepared by mixing 1 mg of synthesized materials with 5 μl of Nafion (5 wt %) solution and 1 ml of water. The mixture was sonicated for an hour and 3 μl of this ink was drop cast on the GCE and dried at room temperature.

3 Results and discussions

3.1 Structure and composition studies

The wide-angle XRD analysis was performed for all the synthesized materials to identify crystal structure (Fig. 1a).

The OMC material exhibited two defined XRD peaks at 2θ values at around 23° and 43° , which strongly signifies (002) and (100) plane of graphitic carbon [38]. These peaks confirm the nano-casting method of synthesis lead to a perfect carbon material. The synthesized pure MoS_2 material exhibited multiple XRD peaks at 2θ 14.8, 33, 40 and 59° correspond to (002), (100), (103) and (110) planes of a hexagonal phase of MoS_2 [JCPDS no- 37-1492] respectively. MoS_2 -OMC possess weak XRD peaks in addition to OMC confirmed the composite material formation. The XRD pattern of the OMC in the MoS_2 -OMC composite illustrated that the addition of Mo, S precursors and hydrothermal heat treatment doesn't alter the peak position. However, the diminished peak intensity of OMC and MoS_2 was observed. The reason behind is the addition of MoS_2 on the surface of OMC may cover the possible surface and hence reduces the well intense (002) plane intensity. Also, due to the vast surface area of the OMC, the formed MoS_2 exhibits diminished size with fine dispersion. To quantify the particle size of the MoS_2 using the Scherrer equation, the major peak (002) was taken into the account. The result illustrated that the crystallite size of (002) peak is

Fig. 1 a X-Ray diffraction pattern b Raman spectroscopy c, d XPS analysis of synthesized materials

1.056 nm for bare MoS_2 . Meanwhile, the major plane of MoS_2 in the composite was not very pronounced due to the formation of small-sized nanoparticles on the surface of OMC. Hence, it is encountered difficulties in calculating the average crystallite size. The experimental error to the WAXS was carried for MoS_2 . The result illustrated that there is a minor experimental error when compared with the standard pattern. The error values in the angstrom unit ($\text{\AA}$) are given in the closed brackets $a = 3.1612(3)$, $b = 3.1612(3)$, and $c = 12.2985(4)$. Raman spectroscopy of OMC and MoS_2 -OMC materials were recorded to identify the unique Raman feature and formation of additional functional groups on the porous carbon by MoS_2 (Fig. 1b). The spectra clearly showed two predominant peaks at 1593 and 1340 cm^{-1} for both OMC and composite materials. The peak centered at 1593 cm^{-1} corresponds to graphitic (G band), occurred by the vibrations of $\text{C}=\text{C}$ bonds in a 2D hexagonal lattice and peak at 1340 cm^{-1} associated with defects and disorders in the structures in carbon materials (D band) [39]. The possible chemical states of the synthesized materials were analyzed by XPS, shown in Fig. 1c, d. The Mo XPS peaks demonstrated two peaks at 229.1 and 232.2 eV , corresponds to $\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$, of Mo^{4+} state. In addition to the Mo^{4+} , two small peaks at around 226 and 236 eV attributed to $\text{S } 2s$ and Mo^{6+} state. Meanwhile, XPS peaks of $\text{S } 2p$ indicated two high intense peaks at the binding energy value of 161.5 and 163.6 eV corresponds to $\text{S } 2p_{3/2}$ and $2p_{1/2}$. From the XRD, Raman

and XPS analysis results illustrate that all the materials exhibit its characteristic nature.

The morphology of SBA-15, OMC, MoS_2 and MoS_2 -OMC were analyzed using FE-SEM and TEM analysis (Figs. 2 and 3). FE-SEM image of mesoporous SBA-15 illustrated a wheat-like structure (Fig. 2a) and a similar structural feature was also observed in the case of OMC materials (Fig. 2b). This observation indicated the formation of thriving porous carbon materials. MoS_2 materials showed flower-like morphology with a large number of sheets connected (Fig. 2c). In the case of MoS_2 -OMC both wheat (OMC) and flower (MoS_2) like structural observation confirming the formation of perfect composite materials (Fig. 2d). TEM analysis was performed to confirm in detailed structural information of the synthesized materials (Fig. 3a–d). The recorded images indicated that a well-defined porous nature of carbon material with numerous MoS_2 flowers existing on its surface. The size varied MoS_2 , with many exposed sheets were well decorated on the porous carbon was seen from the composite TEM image. In our previous work, a similar trend of size varied MoS_2 formation over the interconnected porous carbon was observed [40]. The particle size distribution of MoS_2 in the composite material was calculated and shown in the histogram (Fig. 3d). These results illustrated that averages mean diameter of the MoS_2 exists on the OMC surface is equal to $0.44\text{ }\mu\text{m}$.

Fig. 2 FE-SEM images of **a** SBA-15, **b** OMC **c** MoS_2 and **d** MoS_2 -OMC

Fig. 3 TEM images of **a** OMC, **b** MoS₂-OMC and **c** Isolated MoS₂ and **d** Particle size distribution

3.2 Electrochemical characterization of the synthesized materials

To verify the surface sensitivity of the electrodes, an inner-sphere electrochemical [Fe(CN)₆]^{3-/4-} redox probe is widely used to characterize the electrochemical characteristics of the synthesized materials. Figure 4a shows the comparison of cyclic voltammetric (CVs) responses in 0.1 M KNO₃ solution containing 5 mM of [Fe(CN)₆]^{3-/4-} at a scan rate of 50 mV/s for different synthesized material modified GCE. CV at bare GCE showed a redox peak with a peak potential difference (ΔE_p) of 125 mV indicating a quasi-reversible redox reaction. However, the CV obtained using MoS₂/GCE does not exhibit any redox behavior under similar experimental conditions. But OMC/GCE showed high capacitive behavior with decreased peak potential difference (ΔE_p) of 90 mV.

However, MoS₂-OMC/GCE showed well-defined redox behavior with a decreased peak to peak potential difference (ΔE_p) of 77 mV. Besides, enhancement of 1.5 times of peak current is also observed compared to the bare GC electrode. Figure 4b shows the real and imaginary parts of the impedance spectra represented as Nyquist plots (Z_{im} vs. Z_{re}) for bare, MoS₂, OMC and MoS₂-OMC/GCE's recorded in 0.1 M PBS (pH 7) containing 5 mM [Fe(CN)₆]^{3-/4-}. From

the best-fitted model, the charge transfer resistance (R_{ct}) values were calculated. In Fig. 4b, bare GCE exhibited enlarged semicircle with an R_{ct} value of 1423 Ω , indicating the sluggish kinetic process. The R_{ct} value observed at MoS₂/GCE and OMC/GCE electrode are 336 Ω and 125 Ω respectively. However, as shown in figure MoS₂-MC/GCE doesn't show any well-defined semicircle in the examined frequency range, instead of a slightly curved line indicating the diffusion-limited process with an R_{ct} value of 5 Ω . These mutual results confirmed that MoS₂-OMC composite has good electron transfer ability at the interface.

3.3 Electrochemical determination of hydrazine

The electrochemical properties of the MoS₂-OMC material were investigated using CV experiments. The 0.1 M PBS is used to elucidate the electron transfer characteristics of the material in a three-electrode configuration. The capacitance value of the electrode (C_o) was derived from cyclic voltammograms in 0.1 M PBS [Fig. 5a] using the relationship $CCV = i/(sv)$. Here, CCV is the capacitance (F cm⁻²), 'i' is the average charge or discharge current (A), 's' is the active electrode surface area (cm²), and 'v' is the scan rate (Vs⁻¹). The double-layer capacitance of bare GCE, MoS₂-OMC material modified electrodes were

Fig. 4 **a** CVs obtained for **(a)** Bare GCE, **b** MoS₂/GCE, **c** OMC/GCE, and **d** MoS₂-OMC/GCE in presence of 5 mM [Fe(CN)₆]^{3-/4-} in 0.1 M KNO₃ electrolyte at scan rate 50 mVs⁻¹ **b** Nyquist plots of respective

materials modified GCE and bare GCE **c** Nyquist plots of MoS₂-OMC alone in 0.1 M KNO₃ solution containing 5 mM [Fe(CN)₆]^{3-/4-} (1:1)

calculated from the CV curves and the values are 128 and 365 μF cm⁻² respectively. Interestingly, the MoS₂-OMC/GCE showed a capacitance value of 365 μF cm⁻², which is three-fold higher than that of GCE. As discussed earlier, the MoS₂ and sp²-hybridized structure of carbon might contribute to the high capacitance value in the composite structure. The MoS₂ material with carbon may serve as a promising material for novel functionalized electrodes and supercapacitor applications. To evaluate the electrochemical sensing ability of MoS₂-OMC/GCE for hydrazine oxidation, CV experiments were performed. All other electrodes MoS₂/GCE, OMC/GCE, and bare GCE were also evaluated in the presence of 1.5 mM hydrazine (Fig. 5b). A very small oxidation peak at 0.8 V was observed for bare GCE indicated minimal electrochemical behavior at high overpotential. The CV curve obtained for OMC/GCE also showed a large overpotential with a drawn-out peak at about 0.38 V, though the current response slightly increased compared to the bare GCE. However,

significant small overpotential 0.15 V was observed compared to bare GCE, with an increase in the peak current of 50.4 μA for MoS₂/GCE. In the case of MoS₂-OMC/GCE, a sharp oxidation peak was observed at 0.381 V. The peak current was about two times higher than that of bare GCE. The overall 0.42 V negative shift of the peak potential indicated the catalytic activity of the electrode with the following order MoS₂-OMC/GCE > MoS₂/GCE > OMC/GCE > bare GCE. The reversibility of the electron transfer process and surface accumulation of the electroactive species led to an increased current response.

3.3.1 Scan rate effect

The scan rate effect of MoS₂-OMC/GCE was studied in the potential range from 20 to 100 mVs⁻¹ using a 0.1 M PBS containing 1 mM hydrazine (Fig. 6a). The results illustrated that the positive potential current increases linearly with the square root of the scan rate, also the peak potential

Fig. 5 **a** CV response of Bare GCE **a** MoS₂-OMC modified GCE **b** in 0.1 M PBS alone at a scan rate of 50 mVs⁻¹. **b** CVs of 1.5 mM hydrazine contain 0.1 M PBS (pH 7.0) at bare GCE **a** MoS₂/GCE **b** OMC/GCE **c** and MoS₂-OMC/GCE **d** Scan rate: 50mVs⁻¹

shifted slightly towards the positive direction with the scan rate. The diffusion-controlled kinetics was confirmed by the linear changes of peak current with the square root of the scan rate ($v^{1/2}$), ($R^2 = 0.99$). This is due to the different entities of mesoporous carbon and MoS₂ exhibited on the GCE surface. The fast electron transfer in MoS₂ and better electrochemical behavior were also reported due to the presence of sharp edge plane in MoS₂ catalyst materials. Thus, it is concluded that fast electron transfer kinetics of these materials could be attributed to the presence of sharp edges of composite materials. Furthermore, linear behavior between the plots of log current versus log scan rate with a gradient value of 0.34 (Fig. 6c) confirmed the pure diffusion-controlled process [41].

Based on the voltammetric response, it is expected that amperometric detection of hydrazine by MoS₂-OMC/GCE is a promising approach. An enhanced current value will be observed from the amperometric analysis under stirred conditions was expected. This can be used to estimate the lower limit of detection of hydrazine. Figure 7a illustrated the typical amperometric experiments with successive addition of hydrazine, under conditions at which the potential of MoS₂-OMC/GCE was kept at 0.38 V vs. Ag/AgCl. The result indicated that a well-defined hydrazine oxidation pattern was observed during the successive addition of 1 μ M of hydrazine. The current value is increased with hydrazine concentration (Fig. 7b). The obtained calibration plot was linear for a wide concentration range of 1–9 μ M with a slope value of 0.27 μ A/ μ M (sensitivity) and a correlation coefficient (R^2) of 0.99. The detection limit was found to 0.4 μ M where the signal to noise ratio is observed as 3.

3.3.2 Interference study

Non-enzymatic electrochemical determination of hydrazine using MoS₂-OMC/GCE has not reported so far. The revealed electrocatalytic results of the prepared composite materials are quite interesting for the development of a novel sensor matrix for hydrazine determination. However, a real-time problem is the interference effect during the determination. The well-known interfering compounds such as nitrate, ammonia, and other cations which are all often accompanying with hydrazine. Meanwhile, lowering the detection potential of hydrazine might be the right choice for minimizing the interference effect. Therefore, the inference effect of the modified electrode was performed with a three-fold higher concentration of Na⁺, Ca²⁺, Ni²⁺, Cu²⁺, NH₃, Nitrate, and H₂O₂. Interestingly, the composite electrode does not show any significant electrochemical performance with the interfering molecules (Fig. 8).

3.3.3 Stability and reproducibility of MoS₂-OMC/GCE

The stability of the fabricated sensor platform is an important parameter for deciding the sensor activity. The stability of MoS₂-OMC/GCE was examined for 2-weeks. All the prepared samples were stored in 0.1 M PBS (pH-7.0) at 4 °C. The electrochemical sensing results illustrated that a remarkable constant current response was reported for everyday use. Therefore, it is concluded that under the experimental conditions, the developed sensor showed good reproducibility and prolong stability. The constant stability of the electrode is correlated with the composite MoS₂-OMC structure. The increased surface and nanoporous nature of OMC inferred an enhanced formation

Fig. 6 **a** CV response of $\text{MoS}_2\text{-OMC/GCE}$ in the presence of 1 mM hydrazine at different scan rate ranges from 20–100 mVs^{-1} **b** Corresponding peak current vs. square root of scan rate ($v^{1/2}$), **c** Plot of $\log I_p$ vs $\log v$

Fig. 7 Amperometric determination of hydrazine at $\text{MoS}_2\text{-OMC}$ modified GCE

of active MoS_2 species, which is the main route cause for the enhanced electron transfer processes. To validate the reproducibility of the composite electrode a series of repetitive measurements were also carried out in 1 mM

hydrazine solution. The obtained relative standard deviation (R.S.D.) of 4% for 20 replicate determinations for hydrazine indicated that the electrodes exhibited well characteristic sensing behavior.

Fig. 8 The amperometric response of MoS₂-OMC/GCE for 10 μM hydrazine and three-fold concentration of different interfering species Na⁺, Ca²⁺, Cu²⁺, hydrogen peroxide, nitrate and ammonia in 0.1 M PBS (pH = 7)

4 Conclusions

The present work describes the development of an electrochemical sensor for hydrazine detection using MoS₂-OMC nanocomposite material. Surface analytical tools revealed the existence of the vast surface of OMC facilitated the dispersion of Mo and S precursors. It allowed the growth of MoS₂ in well-isolated spaces of vast surface edges. In an electrochemical environment, the targeted molecule freely coordinated on the surface and rapidly interacts while applying the set potential. The present nanocomposite exhibited an impressive electrochemical activity and maybe the choice of electrode material for sensing hydrazine molecules.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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