Nanocomposite Synthesis of Nanodiamond and Molybdenum Disulfide

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Abstract: A chemically conjugated nanodiamond (ND)/MoS$_2$ nanocomposite was synthesized with amine-functionalized MoS$_2$ and acyl chloride-coordinated ND. The chemical structure and morphology of the nanocomposite were characterized to examine the dispersion of MoS$_2$ on the ND platform. The results revealed that the degree of dispersion was enhanced with increasing ratio of MoS$_2$ nanosheets to ND. Moreover, the nanosheets consisted of several molecular interlayers that were well-dispersed on the ND platform, thereby forming a nanophase. The efficient electrocapacity of the ND/MoS$_2$ nanocomposite was considerably greater than that of the MoS$_2$ electrode alone. Furthermore, the nanophase distribution of MoS$_2$ on ND with a graphitic shell provided a large surface area and reduced the diffusion distance of ions and electrons. Therefore, the nanophase electrode showed higher electrochemical capacitance than that of the MoS$_2$ electrode alone.

Keywords: nanocomposite; MoS$_2$; nanodiamond

1. Introduction

Numerous novel materials and composites including two-dimensional (2D) materials have been exploited with the aim of enhancing electrocapacity, which can be applied for biosensing platforms and electrocatalytic performance. A 2D layered material can be defined as an unsupported crystalline solid with molecular layer thickness characterized by intralayer storage for heat, charge, and light transport [1–4]. This transport occurs in the presence of intralayer covalent bonds and intercalation-based interaction [5]. Specifically, MoS$_2$ as a 2D transition metal dichalcogenide (TMD) exhibits the unique characteristic of charge confinement in the 2D layer in the absence of interlayer interaction along the z-axis [6]. Functional features of 2D MoS$_2$ layers include high thermal and chemical stability for functionalization [7,8], large surface area [4], good mobility [9], and intercalation-based physical interaction [10,11]. For final functional performance, the construction of an electrode and nanophase distribution of an aggregation-free 2D MoS$_2$ molecular layer are critical to induce maximal functional features.

Carbon-based materials including fullerenes, graphene, and carbon nanotubes, are considered as fundamental platform materials of energy conversion and storage, owing to their thermal stability, conductivity, and mechanical properties [12–15]. Furthermore, the electron buffering capability of these materials stems from their high surface-to-volume ratio and the unsaturated carbon bonds. Physicochemical characteristics can reduce oxygen adsorption on a catalyst surface, thereby improving the material performance. In general, the porous structure of carbon materials is characterized by a multiscale nanocage and a high surface-to-volume ratio that provide electron transfer and electrocatalytic active sites. These advantages have often been applied to nanocomposites with metal to induce synergistic functional effects, including solar cells, batteries, and supercapacitors [16–20].
Nanodiamonds (NDs) among carbon platforms have received less attention than some of the other carbon materials due to the high costs and low conductivity of these materials as electric functional materials [21,22]. However, NDs possess excellent physical properties, including high adsorption [23], high surface-to-volume ratio [24], chemical modality on the graphitic shell surface [25], and a nanocage within agglutinate [26]. Moreover, the dispersive capability of NDs in aqueous environments makes it possible to integrate and to extend materials to other functional employment, including biomedical applications as well as electronic functions [27]. NDs serve as a supporting platform that can augment the functional efficiency of the other incorporated pair of 2D materials.

Therefore, in this study a ND/MoS$_2$ nanocomposite by subsequent functionalization was synthesized and characterized. An ND with a graphitic shell around its surface provides stable sites for chemical modification. Immediate chemical reaction between the acyl chloride of NDs and amine-functionalized MoS$_2$ was intended to form aggregation-free MoS$_2$ nanosheet dispersion on the ND support (Scheme 1). This nanophase dispersion of MoS$_2$ in several interlayers on the ND platform was examined from the viewpoint of physical characteristics and potential electrofunctionality.

Scheme 1. Schematic showing conformation of the nanodiamond (ND)/MoS$_2$ nanocomposites.

2. Experimental Methods

2.1. Nanocomposite Formation of MoS$_2$ and Nanodiamonds

ND-COOHs (40 mg) gifted from Nanoresource (Seoul, Korea) were mixed with 100 mL of thionyl chloride (Samcheon Chemical Co., Seoul, Korea) and 0.5 mL of dimethylformamide anhydrous (DMF) in a 250 mL round-bottomed flask. The ND-COOHs were well-dispersed for 15 min of bath sonication under an ice bath. The ND dispersion for acylation was stirred for 24 h at 70 °C under a N$_2$ purge. After reaction, the dispersion was washed repeatedly five times with tetrahydrofuran anhydrous (THF) and the NDs, separated by centrifugation, were dried at 60 °C in an air-circulated oven.

For exfoliation, the mixture of pristine MoS$_2$ (120 mg, <2 µm; Sigma-Aldrich Chemicals, St Louis, MO, USA) and N-vinyl-2-pyrrolidone (60 mL) was sonicated with condition of 55% power amplitude and 3 s pulse (VC750, Sonics Vibra-cell) for 8 h under circulation at 7 °C [28]. After exfoliation, the large MoS$_2$ was separated by centrifugation (4000 rpm, 5 min), and the supernatant was extracted. This supernatant was then filtered through a syringe filter (0.45 µm, HP045AN, Advantec, Taipei, Taiwan) and centrifuged (14,600 rpm, 10 min). Afterward, the settled MoS$_2$ nanosheets were washed with isopropanol and centrifuged repeatedly until the yellow color of N-vinyl-2-pyrrolidone became colorless. The nanosheets were then dried for 24 h at 40 °C under vacuum.

The MoS$_2$ nanosheets (1 mg/mL) were dispersed in DMF. For chemical conjugation, 200 µL of cystamine (5 mg/mL) in DMF was added to 1 mL of the MoS$_2$ dispersion. This dispersion mixture was then sonicated for 1 h under an ice bath. After sonication, the mixture was left to stand at room
temperature for 24 h. Then, functionalized MoS$_2$ was washed repeatedly three times with DMF, separated by centrifugation at 14,600 rpm, and completely dried at 60 °C in a vacuum oven.

Acylated NDs (1 mg/mL) and amine-functionalized MoS$_2$ nanosheets in DMF were dispersed with 5 min of bath sonication. The dispersion of acylated ND and amine-functionalized MoS$_2$ with desired ratios (1:1, 1:2, 1:4, and 1:8) was mixed by sonication under an ice bath for 30 min, and shaken with a vortex for 24 h. After the reaction, the composite was washed and completely dried at 60 °C in a vacuum oven.

2.2. Characterization of ND/MoS$_2$ Nanocomposites

The ultraviolet (UV) absorption of ND-COCl, MoS$_2$ nanosheet, and ND/MoS$_2$ nanocomposite was measured with a V-670 UV-Vis/NIR spectrophotometer (JASCO Corp., Tokyo, Japan). These measurements were performed under the following conditions: scanning speed: 200 nm/min, data interval: 1 nm, UV-Vis bandwidth: 1.0 nm, near-infrared (NIR) bandwidth: 2.0 nm, and wavelength: 350–900 nm [29]. The dispersions (0.2 mg/2 mL) of the nanosheets and the nanocomposite in deionized (DI) water were placed, respectively, in a synthetic quartz cuvette (light path: 1 cm, Hellma Analytics, Müllheim, Germany). Measurement of Fourier transform infrared spectroscopy (FT-IR; Nicolet 6700, Thermo Scientific., Waltham, MA, USA) ranged from 4000–500 cm$^{-1}$ of wavelength and was performed subsequently on the chemical reactant, ND, and MoS$_2$. IR samples were prepared using the standard method of KBr pellet (7 mm in diameter). The materials of 0.5–1 mg were added with a portion of KBr (7 mg).

X-ray photoelectron spectroscopy (XPS; ThermoFisher Scientific Co., Waltham, MA, USA) measurements were also conducted with an Al Kα energy source. The spectra were analyzed using Avantage software (version 1.6, Thermo Fisher Scientific, Waltham, MA, USA). Transmission electron microscopy (TEM) images were obtained with a JEM-2100F electron microscope (JEOL, Tokyo, Japan). For sample preparation, 10 µL each of ND, MoS$_2$, and ND/MoS$_2$ nanocomposite was dropped on Formvar/Carbon on a 200 mesh grid (TED PELLA Co., Redding, CA, USA.) and dried for 10 min at 60 °C in an oven.

2.3. Cyclic Voltammetry (CV) Measurements

A dispersion of ND/MoS$_2$ nanocomposite (1 mg/mL) was prepared in Nafion solution (0.5% in DI water) for electrode fabrication. Dropets of the dispersion (10 µL) were placed on the glassy carbon working electrode (diameter 3 mm) and dried at 80 °C for 1 h. Cyclic voltammetry (CV) measurements (potential: −0.8 to 0.2 V, scan rate: −0.2 to 1.0 V) were performed using a three-electrode system (reference electrode: Ag/AgCl, counter electrode: platinum wire (57 mm in length, OD 0.5 mm), working electrode: ND/MoS$_2$ or MoS$_2$ deposited glassy carbon electrode). Two sets of measurements using a potensiostat (DY2322, Digi-Ivy, Austin, TX, USA) were also performed at potentials ranging from 0.05 to 0.5 V·s$^{-1}$ and scan rates of 0.05, 0.1, and 0.5 V/s. The corresponding CV plots were recorded in a 0.1 M KOH solution (15 ml). Five cycles in 2 sets were performed to obtain a voltamogram. After stabilization from repeated cycles, an oxidation and reduction curve in each second set of a working electrode was shown for data presentation.

3. Results and Discussion

UV–vis absorption spectra were obtained for the MoS$_2$ nanosheets, ND-COCl, and ND/MoS$_2$ nanocomposite with ratios of 1:1, 1:2, 1:4, and 1:8 (Figure 1). Typical MoS$_2$ excitation absorption peaks, which occurred at 630 and 690 nm, were attributed to the direct gap transitions at the K point [30–32]. These indicate the lowest optical band gap of the MoS$_2$ nanosheets (i.e., ~1.8 eV) that were changed, owing to the quantum confinement in the sheets. Changes in the UV absorbance were evaluated for the MoS$_2$/ND nanocomposite with ratios of 1:1 to 1:8. The optical absorbance peaks of MoS$_2$/ND nanocomposite appeared in the same region as those of the MoS$_2$ nanosheets. It was indicated that chemically conjugated MoS$_2$/ND nanocomposite maintained the optical characteristics
of the nanosheets. The intensity of the bands in the spectra were augmented with the increasing ratio of the nanocomposite, as shown in Figure 1 [33].

![Figure 1. UV–vis absorbance spectra of MoS$_2$ nanosheets, ND, and ND/MoS$_2$ nanocomposites with ratios of 1:1, 1:2, 1:4, and 1:8.](image)

Chemical conjugation of the nanocomposite and functional groups of intermediate products was characterized via FT-IR spectroscopy to identify sequential chemical modification of the acyl chloride comprising ND (ND–COCl), MoS$_2$-NH$_2$, and MoS$_2$/ND nanocomposites (Figure 2). The oxidative treatment formed a carbonyl group (C=O) and a hydroxyl group (-OH), occurring as absorption peaks at 1718 and 3400 cm$^{-1}$ on the surface of the carboxylated ND, respectively. The graphitic shell around the crystalline ND was attributed to the absorption bands associated with C=C bond bending at 1625 cm$^{-1}$. After acyl chlorination, ND with an acyl chloride bond (C-Cl) was formed, corresponding to the stretching peak at 593 cm$^{-1}$, whereas no peak for ND-COOH was observed [34]. The results indicated that the carboxylated ND surface was activated by the acyl chloride group for an amine reactive reaction. The functionalization of MoS$_2$ with cysteamine hydrochloride was characterized with comparison of the cysteamine hydrochloride. For the amine-functionalized MoS$_2$, an N–H deformation vibration peak and an NH$_2$ stretching vibration peak, derived from the chemical conjugation with cysteamine hydrochloride, occurred at 1604 and 3390 cm$^{-1}$, respectively [35]. This indicated the successful modification of amine-functionalized MoS$_2$, where amine groups were positioned on the surface of MoS$_2$ nanosheets. The formation of an amide bond (NHCO) between the acyl chloride of ND and the functionalized MoS$_2$ nanosheets was confirmed via FT-IR spectroscopy of the ND/MoS$_2$ nanocomposites. The spectra obtained for the nanocomposites exhibited characteristics of both ND-COCI and the functionalized nanosheets. The absorption bands associated with the ND/MoS$_2$ peak were attributed to hydroxyl bond stretching and an amide bond (NHCO) at 3400 cm$^{-1}$ and 1632 cm$^{-1}$, respectively. Furthermore, the relatively strong absorbance band region resulted probably from the overlapping of bands associated with C=C vibration and C=O stretching [36,37].
The chemical structure of the ND/MoS$_2$ nanocomposite, compared with that of ND-COCl, was determined from the measured XPS spectra, as shown in Figure 3a–f. The C1s peaks of ND-COCl and ND/MoS$_2$ were deconvoluted into four component peaks using Gaussian fitting at 284.8 (C-C), 286.0 (C-O), 287.2 (C=O), and 289 (-COOH) eV, respectively [38,39]. The C=O peak at 287.2 eV for ND-COCl was generated from both acyl chloride and some portion of the carboxyl group. The C=O peak at 287.2 eV arose from the amide group after chemical conjugation of ND/ND/MoS$_2$ nanocomposites. After chemical conjugation between ND-COCl and amine-functionalized MoS$_2$, the intensity of the peak at 286.0 V (C-O) increased significantly relative to that of the peak at 287.2 V (C=O). The results indicate that unreacted acyl chloride would decompose into carboxyl groups during the washing process and from contact with moisture. The O1 peaks of ND-COCl and ND/MoS$_2$ at 531.8 and 533.1 eV were attributed to C=O and COC/COH, respectively. The intensity of the ND/MoS$_2$ peak increased relative to that of the ND-COCl peak, indicating that the unreacted acyl chloride group was converted to the carboxyl group after chemical conjugation with the MoS$_2$ nanosheets (Figure 3b,e). The Cl 2p peaks of the ND-COCl were deconvoluted into two conventional binding energies of 200.3 eV (Cl 2p$_{3/2}$) and 201.9 eV (Cl 2p$_{1/2}$). This indicated that ND-COOH was functionalized by an acyl chloride group on the surface [36]. Deconvolution of the Cl 2p peaks, corresponding to ND/MoS$_2$ generated peaks at 200.3 eV (Cl 2p$_{3/2}$) and 201.9 eV (Cl 2p$_{1/2}$), have resulted from the physical adsorption of remnant chloride ions onto the ND surface and nanocage [34,36].

Figure 4 shows the XPS spectra of the MoS$_2$ and ND/MoS$_2$ nanocomposite. Two strong peaks for the Mo 3d peak of MoS$_2$ are observed at 229.85 for doublet Mo 3d$_{5/2}$ and 232.98 eV for and Mo 3d$_{3/2}$ (Figure 4a). The peaks, corresponding to the S 2p$_{1/2}$ and S 2p$_{3/2}$ orbital of divalent sulfide ions ($S_2^-$) occur at binding energies of 163.85 and 162.65 eV, respectively, as shown in Figure 4b. The results are consistent with the values reported for a MoS$_2$ crystal [35,40–42]. The XPS spectra of ND/MoS$_2$ also revealed typical MoS$_2$ crystalline characteristics with chemically induced shifting. Furthermore, the peak position moved from 229.85 to 229.53 eV for Mo 3d$_{5/2}$ and from 232.98 to 232.64 eV for Mo 3d$_{3/2}$, respectively. Chemically induced shifts were also observed for ND/MoS$_2$ S 2p, with the peaks shifting from 162.65 to 164.44 eV for S 2p$_{3/2}$ and 163.85 to 163.71 eV for S 2p$_{1/2}$ peaks [43]. This indicated that the chemical shift of the ND/MoS$_2$ nanocomposite to lower binding energy than that of MoS$_2$ resulted from chemical conjugation with ND.

Figure 2. FT-IR spectra of the MoS$_2$ bulk, cysteamine, amine-functionalized MoS$_2$ (MoS$_2$-NH$_2$), carboxylated ND, acyl chloride of ND, and ND/MoS$_2$ nanocomposite with ratio of 1:1.
Figure 3. Spectra obtained via X-ray photoelectron spectroscopy. The spectra show the C1s peaks, O1s peaks, and Cl2p peaks, respectively, of the (a)–(c) ND-COCl and (d)–(f) ND/MoS2 nanocomposites.

Figure 4. Spectra obtained via X-ray photoelectron spectroscopy. The spectra show Mo 3d peaks and S 2p peaks of the (a)–(b) MoS2 nanosheets and (c)–(d) ND/MoS2 nanocomposites.

The morphologies of MoS2, ND, and ND/MoS2 nanocomposites (Figure 5) were evaluated with TEM. The MoS2 nanosheets was featured as average size of 300–400 nm along the long axis (Figure 5a,b). The MoS2 nanosheets had a crystalline structure, and several molecular layers were stacked or folded in a planar form [44]. Furthermore, the NDs were well-dispersed with small agglutinins ranging from 80 to 200 nm (Figure 5c,d). The ND/MoS2 nanocomposite with chemical conjugation showed morphological
features that several molecular layers of thin MoS$_2$ nanosheet enveloped ND agglutinins (Figure 5e–h). Amine-functionalized MoS$_2$ nanosheets and NDCOCls were chemically reacted through surface contact, suggesting that the ND/MoS$_2$ nanocomposite was successfully synthesized (Figure 5e–h).

Figure 5. FE-TEM image of (a)–(b) MoS$_2$ nanosheet, (c)–(d) ND, and (e)–(h) ND/MoS$_2$ nanocomposites.

Cyclic voltammograms of the MoS$_2$ nanosheet and ND/MoS$_2$ are shown in Figure 6a–f. For both electrodes, the rectangularity of the CV plots decreased slightly, corresponding to the reversible reactions of Mo$^{2+}$/Mo$^{3+}$ associated with OH$^-$ anions [45]. The possible redox reaction is given as follows [46]:

\[
\text{ND/MoS}_2 + \text{OH}^- \rightleftharpoons \text{ND/MoSOH} + e^-
\]
\[
\text{ND/MoSOH} + \text{OH}^- \rightleftharpoons \text{ND/MoSO} + \text{H}_2\text{O} + e^-
\]

On the same material set, scan rates of 0.05, 0.1, and 0.5 V/s, respectively, and range of potential voltage was differently applied to −0.8 to −0.2 V and −0.2 to 1.0 V. The shape and magnitude of the voltamogram was transitioned from a peak-like shape (Figure 6a–c) to quasi-rectangular shape (Figure 6d–f) depending on the scan rate and potential voltage. The quasi-rectangular shape typically indicates constant and time dependent concentration gradient of an electroactive surface where the electrode radius was typically smaller than diffusion layer [47]. Each CV graph is characterized by a quasi-rectangular shape, consistent with dual behavior, such as the electrical double layer capacitance [48]. MoS$_2$ nanosheets constitute the minimum area of the CV plot, whereas 1:8 and 1:6 ND/MoS$_2$ constitutes the maximum area, which corresponds to the enhanced capacitance. The CV curve of the ND/MoS$_2$ nanocomposites reveals the higher current response and large working area of these composites, compared with those of the MoS$_2$ nanosheet only (Figure 6). The results suggest that the addition of nanodiamonds enhances the electrochemical activity and increases the specific capacitance of MoS$_2$ electrode alone [29,35].

The superior electrical performance of the ND/MoS$_2$ nanocomposite electrode, compared with that of the MoS$_2$ electrode alone, resulted from the unique nanostructure of the composite electrode. Moreover, the large surface area and the nanosized MoS$_2$ phase of the ND/MoS$_2$ composites may have resulted in significant reduction of the diffusion length associated with ion and electron transfer during the oxidation/reduction process. The electrode nanoscale phase makes these composites promising for various applications. Specifically, the NDs acted as nanoscale supports to functionalize synergistically the MoS$_2$ sheets, which served as a three-dimensional highly conductive current collector. The featured architecture of the ND/MoS$_2$ nanocomposites possessing a large specific surface of the electrode...
enables rapid and simultaneous electron and ion transport, thereby leading to excellent electrochemical capacitive performance [42].

Cyclic voltammograms of the MoS2 nanosheet and ND/MoS2 are shown in Figure 6a–f. For both electrodes, the rectangularity of the CV plots decreased slightly, corresponding to the reversible reactions of Mo\(^{2+}/Mo^{3+}\) associated with \(OH^-\) anions [45]. The possible redox reaction is given as follows [46]:

\[
\text{ND/MoS}_2 + OH^- \leftrightarrow \text{ND/MoSOH} + e^- \\
\text{ND/MoSOH} + OH^- \leftrightarrow \text{ND/MoSO} + H_2O + e^- 
\]

On the same material set, scan rates of 0.05, 0.1, and 0.5 V/s, respectively, and range of potential voltage was differently applied to -0.8 to -0.2 V and -0.2 to 1.0 V. The shape and magnitude of the voltamogram was transitioned from a peak-like shape (Figure 6a–c) to quasi-rectangular shape (Figure 6d–f) depending on the scan rate and potential voltage. The quasi-rectangular shape typically indicates constant and time dependent concentration gradient of an electroactive surface where the electrode radius was typically smaller than diffusion layer [47]. Each CV graph is characterized by a quasi-rectangular shape, consistent with dual behavior, such as the electrical double layer capacitance [48]. MoS2 nanosheets constitute the minimum area of the CV plot, whereas 1:8 and 1:6 ND/MoS\(_2\) constitutes the maximum area, which corresponds to the enhanced capacitance. The CV curve of the ND/MoS2 nanocomposites reveals the higher current response and large working area of these composites, compared with those of the MoS2 nanosheet only (Figure 6).

The results suggest that the addition of nanodiamonds enhances the electrochemical activity and increases the specific capacitance of MoS2 electrode alone [29,35].

Figure 6. Cyclic voltammograms of the MoS\(_2\) nanosheet and ND/MoS\(_2\) nanocomposite with ratio of 1:1, 1:2, 1:4, and 1:8. Scan rates of 0.05, 0.1, and 0.5 V/s were employed for potentials ranging from (a)–(c) −0.8 to 0.2 V and (d)–(f) −0.2 to 1.0 V.

4. Conclusions

A chemically conjugated ND/MoS\(_2\) nanocomposite was synthesized with amine-functionalized MoS\(_2\) and acyl chloride-coordinated NDs. The chemical structure and morphology of the nanocomposite were characterized, and the results revealed that the MoS\(_2\) nanosheets were well-distributed on the ND platform, thereby forming a nanophase. Nanophase distribution of MoS\(_2\) on ND with a graphitic shell may provide a large surface area and reduce the diffusion distance of ions and electrons. Therefore, the augmented electrochemical capacitance of the nanophase electrode was induced, compared to that of the MoS\(_2\) electrode alone.

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