Long-Term Stable 2H-MoS₂ Dispersion: Critical Role of Solvent for Simultaneous Phase Restoration and Surface Functionalization of Liquid-Exfoliated MoS₂

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ABSTRACT: Chemical exfoliation approaches such as Li-intercalation for the production of two-dimensional MoS₂ are highly attractive due to their high yield of monolayer forms, cost-effectiveness, and mass-scalability. However, the loss of the semiconducting property and poor dispersion stability in solvent have limited the extent of their potential applications. Here, we report simultaneous phase recovery and surface functionalization for the preparation of a highly stable 2H-MoS₂ dispersion in water. This study shows that high-yield restoration of the semiconducting 2H phase from a chemically exfoliated MoS₂ (ce-MoS₂) can be induced by a mild-temperature (180 °C) solvent thermal treatment in N-methyl-2-pyrrolidone (NMP). In addition to a phase transition, this solvent thermal treatment in NMP realizes concurrent surface functionalization of the 2H-MoS₂ surface, which provides an outstanding dispersion stability to 2H-MoS₂ in water for more than 10 months. Finally, we report the humidity sensor based on the functionalized 2H-MoS₂, which shows a substantial response enhancement compared with a nonfunctionalized 2H-MoS₂ or ce-MoS₂.

INTRODUCTION

Over the past several years, two-dimensional (2D) transition metal dichalcogenides (TMDs) have received a large amount of attention due to their unique electrical, optical, and chemical characteristics compared with their bulk forms.1,7,8 In particular, molybdenum disulfide (MoS₂), which is the most widely investigated semiconducting TMD, is considered a potential substitute of Si for future electronics and optoelectronic devices due to its atomically thin nature and excellent performance such as a high on/off ratio (10⁸), a large carrier mobility (200–500 cm²/V s), and a steep subthreshold swing (70 mV/dec).9,10,11,12 It is considered a potential substitute of Si for future electronics and optoelectronic devices due to its atomically thin nature and excellent performance such as a high on/off ratio (10⁸), a large carrier mobility (200–500 cm²/V s), and a steep subthreshold swing (70 mV/dec).9,10,11,12

Various exfoliation methods for separating stacked layers of bulk MoS₂ to prepare its 2D forms have been developed. Although mechanical exfoliation can produce a high-quality MoS₂ with minimal defects,13–19 extremely low throughput/yield, a limited flake size, and poor thickness control prevent its use for large-scale manufacturing. Thus, massive efforts have been devoted to develop a new method for producing a mass-scale and solution-processible exfoliated MoS₂ through chemical approaches.20–24 Among them, liquid-phase exfoliation in an appropriate solvent assisted by ultrasonication with or without a stabilizer and ion-intercalation method has been established. In particular, lithium-based intercalation is one of the most practical route due to the high yield of the monolayer MoS₂ and mass productivity, meanwhile, the exfoliated MoS₂ processed using the ultrasonication-assisted liquid exfoliation contains a high fraction of thick MoS₂ even over nine layers.8,14–19

Li-intercalation is a promising route for the mass production of high-quality monolayer MoS₂. However, several challenges still remain, although some of the issues of this method have been overcome by ammonia/amine intercalation.20,21 Typically, during a lithiation process, MoS₂ experiences loss of its semiconducting property caused by the structural phase transition from 2H (semiconductor) to 1T phase (metal).14,18,22–26 This 1T phase is known as a metastable phase, and thus the 1T phase can be recovered to the 2H phase by annealing at high temperature typically over 300 °C. Eda and co-workers first reported the successful restoration of the semiconducting property of MoS₂ via annealing after lithiation.14 They systematically studied the phase restoration phenomenon with an elevation of the temperature above 100 °C and confirmed that the restoration to the 2H phase reached ~100% at 300 °C. However, this annealing process was conducted on a substrate after forming a MoS₂ thin film by a casting process, which has associated challenges related to the device stability because such high annealing temperature can result in thermal damage to other components in devices such as flexible substrate or organic semiconductor. Therefore, to widely extend the applicability of the semiconducting MoS₂, it is necessary to develop a solution-phase restoration process. Furthermore, poor dispersion stability of the resultant Li-
intercalated MoS2 upon restacking of the exfoliated MoS2 due to strong van der Waals interactions is a critical issue.27−30 To improve the dispersion stability and avoidance of restacking, proper functionalization of the monolayer 2H-MoS2 surface is essential.31−33 However, most functionalization methods are mainly focused on 1T-MoS2, and it is still challenging to produce a uniformly functionalized monolayer 2H-MoS2 with sufficient solution stability.

Here, we demonstrate the one-step preparation of a highly stable 2H-MoS2 dispersion via solvent thermal treatment in polar solvents using Li-intercalated MoS2. During solvent thermal treatment under mild temperature (180 °C), efficient restoration of the 2H phase is accomplished with an approximately 85% conversion ratio from 1T-MoS2 obtained from a Li-intercalation method. Notably, when the solvent thermal treatment was conducted in N-methyl-2-pyrrolidone (NMP), 2H-MoS2 can be functionalized simultaneously, providing an outstanding long-term stability of a concentrated aqueous dispersion for over 10 months. Moreover, the functionalized 2H-MoS2, which has a high water absorption capability, presents a high sensitivity to humidity, realizing a humidity sensor with an outstanding response activity that is several times higher than that of the original 1T-MoS2 prepared by Li-intercalation method.

■ RESULTS

The overall process for the preparation of a highly stable 2H-MoS2 dispersion is illustrated in Figure 1a. First, few and monolayer MoS2 nanosheets were prepared from the chemical exfoliation of bulk MoS2 via the Li-intercalation method14,22,26 (see Experimental Section for details). After complete washing of the samples to remove the remaining Li ions, the obtained chemically exfoliated MoS2 (ce-MoS2 with majority 1T phase) was transferred to the following polar solvents with a sufficiently high boiling point and suitable dispersion capability for MoS2: ethylene glycol (EG), formamide (FA), propylene carbonate (PC), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetraethylene glycol dimethyl ether (TGDE), and hexamethylphosphoramide (HMPA). During the transfer procedure, the resultant ce-MoS2 should be in a wet-clay state with a small quantity of water to prevent the restacking of MoS2 sheets.5,34 A homogeneous dispersion and

![Figure 1. Schematic of one-step phase recovery and surface functionalization using solvent thermal treatment. (a) Overall process for the preparation of a highly stable 2H-MoS2 dispersion. To chemically exfoliate the MoS2 to a monolayer level, solution-based Li-intercalation using n-butyl lithium was conducted. The resultant ce-MoS2 was solvent thermal treated in various solvents such as N-methyl-2-pyrrolidone (NMP). (b) Photographs showing the dispersion stability of 2H-MoS2 (annealed in NMP) in water after 10 months.](http://example.com/image1.png)
dispersion stability within polar solvents are also important for avoiding the agglomeration of ce-MoS₂ during the solvent thermal treatment. Thus, after ultrasonication for 30 min to obtain a homogeneous MoS₂ dispersion in each polar solvent, the dispersions were kept for 1 week to investigate their stability. Based on this result, EG, FA, PC, NMP, and DMSO were chosen as appropriate solvent media for the solvent thermal treatment (Figure S1 in the Supporting Information).

Previously, several studies have reported that the thermally driven phase transition from 1T to 2H phase was about 100% when the temperature was elevated up to 300 °C. However, structural and chemical defects such as sulfur vacancies, triangular etch pits, and oxidation of MoS₂ were inevitable at such high temperature (about 300 °C). Moreover, it should be noted that the majority (about 80%) of the phase transition has already occurred at 150 °C. Thus, in this study, the thermal treatment was conducted at a relatively low temperature (180 °C) to minimize the formation of structural and chemical defects and to prevent the boiling of the solvent. During the solvent thermal treatment at 180 °C for 5 h, we observed the structural phase transition from 1T (metal) to 2H (semiconductor) phase. In addition, when the solvent thermal treatment was conducted in NMP, the resultant 2H-MoS₂ (MoS₂−NMP) dispersion showed high stability in the aqueous solvent, as shown in Figure 1b.

To investigate the phase transition in MoS₂, an X-ray photoelectron spectroscopy (XPS) analysis was conducted before and after the solvent thermal treatment. All of the XPS spectra were calibrated with reference to the C 1s peak at 284.5 eV to compensate for the charging effect. As depicted in Figure 2a, the XPS spectra of Mo 3d consist of three sets of peaks: (i) MoO₃ peaks (yellow line), which can be deconvoluted into Mo⁶⁺ doublets 3d₅/₂ and 3d₃/₂ located at 232.6 and 235.3 eV, respectively; (ii) the Mo⁴⁺ 3d₅/₂ and Mo⁴⁺ 3d₃/₂ of 1T-MoS₂ peaks (blue line) located at 228.2 and 231.3 eV, respectively, and (iii) the Mo⁴⁺ 3d₅/₂ and Mo⁴⁺ 3d₃/₂ of 2H-MoS₂ peaks (red line) located at 229.0 and 232.1 eV, respectively. The ce-MoS₂ was identified to be metallic 1T phase (71.37%) partially mixed with oxidized MoS₂ (11.35%) (Figure 2a), which is consistent with the findings of previous studies. After the solvent thermal treatment in each polar solvent, the Mo 3d spectra were shifted toward the higher binding energy side because the Mo 3d peaks of 2H-MoS₂ were intensified, as shown in Figure 2b. The ratio of each phase was calculated from the sum of the total area of each peak except the peak of the MoO₃ phase, as presented in Figure 2b. (These data are also provided in Table S1 in the Supporting Information.) In addition, the O 1s spectrum also supports the quantitative analysis results of the MoO₃ phase except the MoO₃−NMP sample containing C=O groups, as shown in Figure S2.

For ce-MoS₂, the 1T phase was dominant and the fraction of 2H phase was only about ~30%. After the solvent thermal treatment, however, the 1T phase was restored to the 2H phase and the 2H phase ratio reached about 80% for all of the polar solvents used for the treatment. Similarly, the phase transition from 1T to 2H was also observed in the S 2p XPS spectra after the solvent thermal treatment, as depicted in Figure S3 in the Supporting Information. From the S 2p spectra, the 2H phase ratio was calculated to be approximately 85% for all of the polar solvents used (Table S1 in the Supporting Information), which is consistent with the calculation results based on the Mo XPS peaks.



Figure 2. Investigation of 1T to 2H phase transition. (a) XPS spectra of ce-MoS₂ and 2H-MoS₂ after the solvent thermal treatment in each polar solvent at 180 °C for 5 h. Deconvoluted red and blue lines represent the 2H-MoS₂ and 1T-MoS₂, respectively. The MoO₃ peaks (yellow line) and S peaks (brown line) are also shown after deconvolution. (b) Calculated 2H phase and MoO₃ ratio from Mo 3d XPS analysis results after the solvent thermal treatment in various solvents. (c, d) Transmission electron microscopy (TEM) images, as depicted in Figure 2c,d. In the high-angle annular dark-field STEM image, the ce-MoS₂ only

Moreover, the Raman spectra of the ce-MoS₂ and MoS₂−NMP were compared, as shown in Figure S4, for a more in-depth characterization of the MoS₂ nanosheets. The Raman spectra from ce-MoS₂ show several bands, J₁, J₂, J₃, E₁g, E₂g, and A₁g, indicating the 1T-phase MoS₂, whereas only E₂g and A₁g peaks were observed for MoS₂−NMP, confirming that it is the 2H phase. The spectrum for MoS₂−NMP shows peaks at 385 and 407 cm⁻¹. Also, from the difference (22.3 ± 1.49 cm⁻¹) of E₂g and A₁g Raman peak positions, the average number of layers was calculated to be slightly over 2, which is consistent with the AFM measurement results shown in Figure S5.

Furthermore, the phase transition from 1T to 2H was identified by high-resolution scanning transmission electron microscopic (STEM) images, as depicted in Figure 2c,d. In the high-angle annular dark-field STEM image, the ce-MoS₂ only
reveals hexagonally oriented Mo atoms because the MoS$_2$ was reconstructed to an ABC ($S\rightarrow Mo\rightarrow S'$) sequence stack and, as a result, the lattice points of S atoms were distorted. After the solvent thermal treatment, the hexagonally arranged S atoms appeared between Mo atoms due to the restoration of the MoS$_2$ structure to an ABA ($S\rightarrow Mo\rightarrow S$) sequence stack. Interestingly, when the solvent thermal treatment was conducted in NMP, the 2H phase ratio showed the highest value and the fraction of MoO$_3$ was lowest (6.44%) among all of the samples, which is similar to the MoO$_3$ fraction in natural bulk MoS$_2$. This can be related to the fact that NMP is also a useful reduction agent for deoxygenating of other 2D materials such as graphene oxide due to its oxygen-scavenging property, and thus these results may originate from the combination of thermal and chemical deoxygenating effects during the solvent thermal treatment. (This will be discussed in detail later.) The recovery from 1T to 2H phase by the solvent thermal treatment is further supported by the re-emergence of the A and B extinction peaks in the UV–vis absorption measurement results shown in Figure 2e. As presented in Figure 2e, no extinction peaks were observed in the extinction spectra of ce-MoS$_2$ within the wavelength range of 550–750 nm due to the dominance of the 1T phase. After the solvent thermal treatment, however, the A and B extinction peaks appeared for the samples treated in all of the polar solvents. The A and B extinction peaks, which are located at 657.01 and 607.77 nm, respectively, originated from the monolayer 2H-MoS$_2$.

Notably, the extinction peaks of the sample annealed in NMP were almost identical to the A and B extinction peaks of pure monolayer MoS$_2$, whereas those of other 2H-MoS$_2$ were slightly red-shifted. (Individual peak positions are presented in Table S2 in the Supporting Information.) Considering that the band gap of MoS$_2$ decreases with increasing thickness of MoS$_2$, these extinction data strongly suggest that the resultant 2H-MoS$_2$ in EG, FA, DMSO, and PC were at least partially agglomerated and thickened during the solvent thermal treatment, whereas few or monolayer MoS$_2$ flakes in NMP were preserved without agglomeration. In addition, to quantify the average number of atomic layers in the MoS$_2$ flakes, an atomic force microscopy (AFM) analysis on the samples was conducted, as shown in Figure S5. MoS$_2$–NMP sheets with an average diameter of 207.9 ± 82.7 nm can be clearly observed in the AFM images. A typical height of 1.2–1.4 nm was obtained using the AFM line profiles and the average number of layers in the flake samples was calculated to be 2.38 ± 0.92, confirming that mono- to few-layer MoS$_2$–NMP was successfully preserved. These results are consistent with the Raman analysis results (Figure S4). Moreover, even after the long-term storage of MoS$_2$–NMP for 10 months, the average diameter was maintained at 218.9 ± 85.7 nm (Figure S6). This is in contrast with the coagulation of MoS$_2$ nanosheets reported previously.
These observations imply the change in the surface chemistry of MoS$_2$ during the solvent thermal treatment using NMP. As depicted in panel (a), the deconvoluted C 1s XPS spectra indicate the formation of C$\equiv$O and C$\equiv$N bonds in MoS$_2$−NMP, which were not present in ce-MoS$_2$. (The XPS spectra were acquired after fully washing the flakes with EtOH, acetone, and deionized (DI) water.) We also checked the N 1s spectra (Figure 3b), where the Mo$^{4+}$ 3p$_{3/2}$ and Mo$^{6+}$ 3p$_{3/2}$ peaks partially overlapped with the N 1s peak. The change in the XPS spectra indicates that, after the solvent thermal treatment in NMP, Mo$^{−}$N bonding was formed and the fraction of Mo$^{6+}$ 3p$_{3/2}$ (from MoO$_3$) decreased from 11.3 to 7.2%. This result is consistent with the XPS analysis results of the Mo 3d peaks shown in Figure 2a and indicates the reduction of MoS$_2$ during the solvent thermal treatment in NMP. Due to the oxygen-scavenging property of NMP during the solvent thermal treatment, NMP can be partially oxidized or decomposed to organic compounds containing an amide group such as N-ethylacetamide, N-methylformamide, or acetamide, which is implied by the color change of NMP from colorless to brown, as shown in Figure S7 in the Supporting Information. It should be noted that these species can be chemisorbed to the surface MoS$_2$. Figure 3b shows that the N 1s XPS spectrum of the solvent-thermal-treated MoS$_2$ in NMP has a noticeable shoulder peak at around 400 eV, which is known to be related to the Mo$\equiv$N bond.

Furthermore, we also investigated the C 1s XPS spectra for the samples obtained with other polar solvents (EG, FA, PC, and DMSO). As shown in Figure S8, the overall C 1s peaks were similar to that of ce-MoS$_2$. This result means that the surface functionalization of MoS$_2$ did not take place in other solvents, which may explain the agglomeration of MoS$_2$ during the solvent thermal treatment. In addition to the XPS results, we also investigated the TEM images and the corresponding energy-dispersive X-ray spectroscopy (EDS) mapping for Mo, S, and N elements on ce-MoS$_2$ and MoS$_2$−NMP. As shown in Figure 3c, the EDS mapping results of ce-MoS$_2$ show the presence of only Mo and S, whereas the EDS results of MoS$_2$−NMP additionally present well-distributed C, O, and N elements (Figure 3d). This result also supports the finding that the MoS$_2$−NMP was uniformly functionalized after the solvent thermal treatment in NMP, although additional agents were not added to the solvent.

To further investigate the surface functionalization of MoS$_2$−NMP, an attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis was performed and the results are shown.
in Figure 4a. After the solvent thermal treatment in NMP, we observed the appearance of strong peaks at 3423, 2917, 2846, 1702, 1433, and 1374 cm\(^{-1}\), which represent the N–H, C–H, C=O, and C–N bonds, respectively. As shown in Figure 5a, these peaks and the overall FTIR spectra of MoS\(_2\)–NMP are well matched with those of acetamide.

The surface-attached molecule was also characterized using the solid-state \(^{13}\)C cross-polarization magic-angle-spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy. As shown in Figure 4b, the NMR spectra for pure acetamide (black) show characteristic chemical shifts (\(\delta\)) corresponding to carbonyl and aliphatic carbons (\(\alpha\)-C in this case) at 179.9 and 25.7 ppm, which are marked with green and blue points, respectively. In the case of MoS\(_2\)–NMP (blue), the peaks corresponding to both \(\alpha\)-C (blue) at 173.5 ppm and carbonyl C (green) at 34.5 ppm, which are comparable with those of pure acetamide. The broad peak at 130.3 ppm was also observed for the nonfunctionalized bulk 2H-MoS\(_2\) (red), suggesting the peak is not related to the surface-functionalized layer. Overall, these NMR, FTIR, TEM, and XPS analysis results confirm that the ce-MoS\(_2\) was restored to 2H-MoS\(_2\) and simultaneously functionalized with acetamide during the solvent thermal treatment in NMP.

The amount of absorbed molecules was characterized by a thermogravimetric analysis (TGA) after completely drying the samples. Figure 4c shows the TGA weight loss curves of ce-MoS\(_2\) and MoS\(_2\)–NMP measured from room temperature to 700 °C under an air atmosphere. The weight loss until 300 °C, which is caused by the evaporation of the absorbed water molecules, was measured to be 2.15 and 3.68% for ce-MoS\(_2\) and MoS\(_2\)–NMP, respectively. In the temperature range from 300 to 500 °C, a major weight loss of 14.35% occurred for ce-MoS\(_2\) which can be explained by the replacement of S by O due to the oxidation of MoS\(_2\) to MoO\(_3\). Overall, a comparison of the TGA curve of ce-MoS\(_2\) with that of MoS\(_2\)–NMP indicates that the additional weight loss of MoS\(_2\)–NMP of about 10% is due to the decomposition of acetamide attached on MoS\(_2\). In addition, the X-ray diffraction (XRD) analyses were conducted to confirm the interlayer spacing (Figure 4d). In ce-MoS\(_2\), we observed the sharp peak at 2\(\theta\) = 14.06°, which corresponds to (002) planes of the Li-intercalated MoS\(_2\). In the case of MoS\(_2\)–NMP, however, the (002) peak was found to be shifted to a significantly lower angle at 2\(\theta\) = 9.04°. This result reveals that the expansion of the lattice spacing along the c axis from 0.629 nm (ce-MoS\(_2\)) to 0.974 nm (MoS\(_2\)–NMP) is due to acetamide molecules attached on MoS\(_2\).

We investigated the long-term stability of the various aqueous dispersions of solvent-thermal-treated MoS\(_2\). The concentration of MoS\(_2\) in the dispersions was estimated using the Beer–Lambert law, \(A = \alpha Cl\), where \(A\) is the measured absorbance at a particular wavelength, \(\alpha\) is the extinction coefficient, \(C\) is the concentration of the dispersion, and \(l\) is the thickness of the solution layer.\(^{10,19}\) We first obtained the extinction coefficient (at \(\lambda = 672\) nm) of each sample by fitting the slope of \(A/l\) as a function of MoS\(_2\) concentration (Figure S10 in the Supporting Information). As shown in Figure S10, similar concentrations of MoS\(_2\) dispersions with 0.75 mg/mL were then prepared, and the absorbance of MoS\(_2\) aqueous dispersion was monitored regularly during 50 days. To enhance the accuracy of this measurement, all of the MoS\(_2\) dispersions were diluted 50-fold before the measurement to minimize the light-scattering effect. As shown in Figure 5a, the MoS\(_2\)–NMP aqueous dispersion showed a superior long-term dispersion stability compared with other dispersion samples. However, during the early-stage storage up to 1 week, ce-MoS\(_2\) and the solvent-thermal-treated MoS\(_2\) in EG (MoS\(_2\)–EG) presented a stable dispersion state, the absorbance of ce-MoS\(_2\) in the supernatant was sharply reduced and reached almost 0 within 20 days, which can be attributed to the fact that the negative surface charge resulting from the Li-intercalation was gradually transferred to the water molecules.\(^{30}\) Other aqueous dispersions obtained by the solvent thermal treatment in EG, PC, FA, and DMSO also showed poor dispersion stability, and a significant portion of MoS\(_2\) was precipitated before 20 days, whereas the aqueous dispersions containing MoS\(_2\)–NMP were still stable even after 50 days. The absorbance of dispersed MoS\(_2\)–NMP (0.2337) is about 39.0 and 16.5 times higher than that of the dispersed ce-MoS\(_2\) (0.006) and MoS\(_2\)–EG (0.0142) after 50 days, respectively. Additional analysis data regarding the dispersion properties of the samples are provided in Figure S10 and Table S3. A photograph of highly stable MoS\(_2\)–NMP is depicted in Figure 5b.
The outstanding dispersion stability of the MoS$_2$−NMP nanosheets is consistent with the measured ζ-potential values (Table S4 in the Supporting Information). The ζ-potential of the chemically exfoliated nanosheets of MoS$_2$ containing a large fraction of 1T phase was $-43.1$ mV due to excess surface charge.$^{33,50,51}$ In general, the surface of bare 2H-MoS$_2$ is not charged, and therefore it cannot be stabilized in common organic solvents because of a low ζ-potential ($-20.2$ mV).$^{24,33}$ However, the ζ-potential ($-41.2$ mV) of the MoS$_2$−NMP functionalized with polar molecules was sufficiently high and can explain the good dispersion stability in water.$^{51,52}$

Considering the dispersion stability in an aqueous solvent (Figure 5), it is expected that the resultant MoS$_2$ after the solvent thermal treatment in polar solvents will have a different surface hydrophilicity. We compared the water contact angle (WCA) of ce-MoS$_2$, MoS$_2$−EG (without functional group), and MoS$_2$−NMP (with acetamide functional group). As shown in Figure S11a, the WCAs were 34.63° for ce-MoS$_2$ and 71.96° for MoS$_2$−EG. These WCAs of ce-MoS$_2$ and MoS$_2$−EG are comparable with the recently reported values of Li-intercalated 1T-MoS$_2$ and mechanically exfoliated 2H-MoS$_2$ from bulk.$^{35,53}$ The substantially lower WCA (20.21°) of MoS$_2$−NMP than that of other samples indicates that the MoS$_2$−NMP has a much higher hydrophilicity, which is consistent with the outstanding dispersion stability in water.

The greater water affinity of MoS$_2$−NMP suggests its potential application to humidity sensor devices. We fabricated a resistance-type humidity sensor using an interdigitated electrode with 4 μm channel width by drop-casting of MoS$_2$−NMP (Figure 6a) to investigate the humidity-sensing properties (see the Experimental Section for details). As shown in Figure 6b, we observed a remarkably different response behavior depending on the functionalization at 80 relative humidity (RH)%. The response of the sensor was calculated by $R_H/R_0$, where $R_H$ is the resistance value in the presence of humidity and $R_0$ is the resistance value when dry air was passed through the chamber. ce-MoS$_2$ and MoS$_2$−EG show a positive response (increase in resistance), and the response of MoS$_2$−EG was higher than that of ce-MoS$_2$ due to the transition from 1T (metal) to 2H (semiconductor) phase. In contrast, the response of MoS$_2$−NMP shows a negative response (decrease in resistance) and its response was much higher than that of other devices. This result can be attributed to the difference in water affinity and the hydrogen bond formation between the carbonyl group and water molecules (Figure 6a, right), as already reported.$^{54}$ The sensor performance was further characterized by adjusting the humidity from 25 to 95 RH%, and the corresponding responses of the three sensors are shown in Figure 6c. Different sensing behaviors depending on functionalization were also detected over the whole range of humidity. The response of ce-MoS$_2$ and MoS$_2$−EG increased...
MoS₂−NMP shows a more rapid increase in response with increasing humidity levels due to hydrophilic functionalization. The sensitivity of MoS₂−NMP was 5 times higher than that of c-MoS₂ at 95 RH% (Figure S11b in the Supporting Information). These results indicate that an appropriate modification of MoS₂ surface combined with a phase transition can improve the device performance to a great extent.

### CONCLUSIONS

In summary, we have demonstrated a practical method for a high-yield phase transition from 1T to 2H phase and simultaneous functionalization of MoS₂ via the solvent thermal treatment in a polar solvent. We found that the solvent thermal treatment in a polar solvent at a mild temperature (180 °C) is appropriate for restoration from 1T (metal) to 2H (semiconductor) phase. In particular, solvent thermal treatment of MoS₂ in NMP was simultaneously and uniformly functionalized with acetamide—a thermal decomposition product of NMP, which was confirmed on the basis of XPS, FTIR, NMR, TGA, and XRD analysis results. This surface functionalization by hydrophilic molecules can provide an excellent dispersion stability of 2H-MoS₂ in water for more than 10 months. Finally, the humidity sensor fabricated using MoS₂−NMP showed a more rapid increase in response with increasing humidity levels due to hydrophilic functionalization. The sensitivity of MoS₂−NMP was 5 times higher than that of c-MoS₂ at 95 RH% (Figure S11b in the Supporting Information). These results indicate that an appropriate modification of MoS₂ surface combined with a phase transition can improve the device performance to a great extent.

### EXPERIMENTAL SECTION

#### Materials.

MoS₂ powder (~6 μm) was purchased from 2D Semiconductor, Inc. A 1.6 M n-butyl lithium solution, ethylene glycol (EG), formamide (FA), propylene carbonate (PC), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetraethylene glycol dimethyl ether (TGDE), and hexamethylphosphoramide (HMPA) were purchased from Sigma-Aldrich.

MoS₂ dispersions in polar solvents were sonicated for 30 min to produce a homogeneous solution before the solvent thermal treatment. After sonication, the MoS₂ dispersion was transferred to a two-neck flask and refluxed at 300 rpm under an Ar flow. A heating mantle was used to heat the MoS₂ dispersion up to 180 °C for 15 min and the temperature was maintained for 5 h without boiling over. The resultant suspension was filtered on the basis of XPS, FTIR, NMR, TGA, and XRD analysis results. This surface functionalization by hydrophilic molecules can provide an excellent dispersion stability of 2H-MoS₂ in water for more than 10 months. Finally, the MoS₂ dispersion was centrifuged with a low rpm (2000 rpm, 5 min; 1000 rpm, 10 min) to remove the agglomeration of MoS₂ during the solvent thermal treatment.

#### Characterization of Phase Transition and Functionalization of MoS₂.

For confirming the phase transition, an X-ray photoelectron spectroscopy (XPS) analysis was conducted using a multipurpose X-ray photoelectron spectrometer (Sigma Probe; Thermo VG Scientific). The absorbance of the MoS₂ dispersion was measured by a UV−vis spectrophotometer (Optizen POP; Mecasys). The FTIR spectra were collected with an attenuated total reflectance FT−infrared spectroscopy (ATR−FTIR, ALPHA-P; Bruker) in the range from 500 to 4000 cm⁻¹. High-resolution-TEM images and EDS mapping were obtained using a double Cs-corrected Titan TEM (Titan G2 60−300; FEI) with 80 kV accelerating voltage and a 200 kV TEM (JEM-2100F; JEOL), respectively. The X-ray diffraction (XRD) measurement was carried out using a multipurpose thin-film X-ray diffractometer (D/Max 2500; Rigaku) and weight loss was measured by thermogravimetric analysis (TGA, Setsys 16/18; Setaram Instrumentation). The AFM characterization was conducted in a noncontact mode using the atomic force microscope (AFM) from Asylum Research Cypher. The solid-state ¹³C (100 MHz) NMR spectra were measured using an Agilent 9.4 T (400 MHz ¹H NMR frequency) spectrometer with a 1.6 mm magic-angle spinning (MAS) probe. All of the reported chemical shifts were referenced to adamantane at 298 K. For cross-polarization (CP) MAS, ¹³C{¹H} NMR spectra were attained with 8 h of signal averaging at 20 kHz MAS, with a constant 50 kHz radio frequency field strength applied to the ¹³C NMR channel during the ¹H−¹³C NMR CP (contact time of 3 ms).

#### Stability Test of MoS₂ Aqueous Dispersion.

Stability of each MoS₂ dispersion was determined by high-magnification microscopy (optical microscope) at pH 11 (HCl) and pH 1 (HCl) for 24 h. The stability test was performed after each MoS₂ dispersion was measured by a UV−vis spectrophotometer (Optizen POP; Mecasys) with a 1 cm path cuvette after 24 h to exclude the aggregated MoS₂. To obtain the concentration of each MoS₂ dispersion, we used the Lambert−Beer law. The concentration changes were monitored during 50 days. To enhance the accuracy, all of the MoS₂ dispersions were measured after dilution to obtain the absorbance below 1. ζ Potential is a surface potential that affects the affinity of the adsorbed ion. The values are reported as an average of three measurements.

#### Fabrication and Measurement of Humidity Sensor.

Water contact angles (WCAs) were obtained by a dynamic contact angle meter (Phoenix 300; SEO) equipped with a digital camera. To fabricate a interdigitated electrode with 4 μm
width on a Si wafer, we used a typical photolithography with AZ5142E photoreist and a mask aligner (MDA-8000B). After the development of the patterns, Au with a thickness of 100 nm was deposited as a source and drained by thermal evaporation. The MoS2 dispersion was then drop-cast on the electrode patterns. The electrical characteristics of the sensors were measured by a digital multimeter (34970A; Keysight Technologies). The humidity-sensing properties were examined by controlling the relative humidity from 25 to 95%. To modify the atmosphere inside the chamber, the mixtures of dry air and water vapor with different mixing ratios were used. In addition, a commercial humidity sensor (testo 608-h2) was installed inside the chamber to obtain the real-time humidity data inside the chamber. The sensing experiments were carried out at an ambient temperature of 25 °C and the total gas flow rate was fixed at 500 cm³/min.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00841.

Dispersion stability of ce-MoS2: high-resolution O 1s XPS spectra; S 2p XPS spectra; Raman spectra; AFM; photographs of solvent-thermal-treated NMP; high-resolution C 1s XPS spectra; FTIR spectra; Lambert–Beer plots; photographs of water contact angle (Figures S1–S11); molar ratio of 1T-MoS2: 2H-MoS2 and MoO3; positions of A and B exciton peaks; calculated concentration of MoS2: ζ potential values (Tables S1–S4) (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

(1) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS2 transistors. Nat. Nanotechnol. 2011, 6, 147–150.

(2) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 2012, 7, 699–712.

(3) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.; J.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 2013, 5, 263–275.

(4) Yin, Z.; Li, H.; Li, H.; Jiang, L.; Shi, Y.; Sun, Y.; Lu, G.; Zhang, Q.; Chen, X.; Zhang, H. Single-Layer MoS2 Phototransistors. ACS Nano 2012, 6, 74–80.

(5) Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multilayer MoS2 Transistors with Scandium Contacts. Nano Lett. 2013, 13, 100–105.

(6) Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive photodetectors based on monolayer MoS2. Nat. Nanotechnol. 2013, 8, 497–501.

(7) Huang, X.; Zeng, Z.; Zhang, H. Metal dichalcogenide nanosheets: preparation, properties and applications. Chem. Soc. Rev. 2013, 42, 1934–1946.

(8) Li, H.; Wu, J.; Yin, Z.; Zhang, H. Preparation and Applications of Mechanically Exfoliated Single-Layer and Multi layer MoS2 and WS2 Nanosheets. Acc. Chem. Res. 2014, 47, 1067–1075.

(9) Yim, S.; Sim, D. M.; Park, W. I.; Choi, M.-J.; Choi, J.; Jeon, J.; Kim, K. H.; Jung, Y. S. Surface-Shielding Nanostuctures Derived from Self-Assembled Block Copolymers Enable Reliable Plasma Doping for Few-Layer Transition Metal Dichalcogenides. Adv. Funct. Mater. 2016, 26, 5631–5640.

(10) Bang, G. S.; Nam, K. W.; Kim, J. Y.; Shin, J.; Choi, J.; Choi, S.-Y. Effective Liquid-Phase Exfoliation and Sodium Ion Battery Application of MoS2 Nanosheets. ACS Appl. Mater. Interfaces 2014, 6, 7084–7089.

(11) Liu, G.; Ma, H.; Teixeira, I.; Sun, Z.; Xia, Q.; Hong, K.; Tsang, S. C. E. Hydrazine-Assisted Liquid Exfoliation of MoS2 for Catalytic Hydrogen Oxidation in 4-Methylphenol. Chem. – Eur. J. 2016, 22, 2910–2914.

(12) Shen, J.; He, Y.; Wu, J.; Gao, C.; Keyshar, K.; Zhang, X.; Yang, Y.; Ye, M.; Vajtai, R.; Lou, J.; Ajayan, P. M. Liquid Phase Exfoliation of Two-Dimensional Materials by Directly Probing and Matching Surface Tension Components. Nano Lett. 2015, 15, S449–S454.

(13) Zhong, J.; Zhang, H.; Dong, S.; Liu, Y.; Nai, C. T.; Shin, H. S.; Jeong, H. Y.; Liu, B.; Loh, K. P. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. Nat. Commun. 2014, 5, No. 2995.

(14) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS2. Nano Lett. 2011, 11, S511–S516.

(15) Stephenson, T.; Li, Z.; Olsen, B.; Mitlin, D. Lithium ion battery applications of molybdenum disulphide (MoS2) nanocomposites. Energy Environ. Sci. 2014, 7, 209–231.

(16) Zhang, W.; Wang, Y.; Zhang, D.; Yu, S.; Zhu, W.; Wang, J.; Zheng, F.; Wang, S.; Wang, J. A one-step approach to the large-scale synthesis of functionalized MoS2 nanosheets by ionic liquid assisted grinding. Nanoscale 2015, 7, 10210–10217.

(17) Nguyen, E. P.; Carey, B. J.; Daeneke, T.; Ou, J. Z.; Latham, K.; Zhuiykov, S.; Kalantar-zadeh, K. Investigation of Two-Solvent Grinding-Assisted Liquid Phase Exfoliation of Layered MoS2 Chem. Mater. 2015, 27, 53–59.

(18) Acerce, M.; Voiry, D.; Chhowalla, M. Metallic 1T phase MoS2 nanosheets as supercapacitor electrode materials. Nat. Nanotechnol. 2015, 10, 313–318.

(19) Coleman, J. N.; Lotya, M.; O’Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H.-Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J.; Donegan, J. F.; Grunlan, J. C.; Moriarty, G.; Shmeliov, A.; Nicholls, R. J.; Perkins, J. M.; Grieveson, E. M.; Theuwissen, K.; McBride, D. W.; Nellist, P. D.; Nicolosi, V. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. Science 2011, 331, 568–571.

(20) Jeffery, A. A.; Nethravathi, C.; Rajamathi, M. Scalable large nanosheets of transition metal disulphides through exfoliation of amine intercalated MS2 [M = Mo, W] in organic solvents. RSC Adv. 2015, 5, S1176–S1182.

(21) Anto Jeffery, A.; Nethravathi, C.; Rajamathi, M. Two-dimensional nanosheets and layered hybrids of MoS2 and WS2 through exfoliation of ammoniated MS2 (M = Mo, W). J. Phys. Chem. C 2014, 118, 1386–1396.

(22) Chou, S. S.; Huang, Y.-K.; Kim, J.; Kaehr, B.; Foley, B. M.; Lu, P.; Dykstra, C.; Hopkins, P. E.; Brinker, C. J.; Huang, J.; Dravid, V. P. Controlling the Metal to Semiconductor Transition of MoS2 and WS2 in Solution. J. Am. Chem. Soc. 2015, 137, 1742–1745.

(23) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L. S.; Jin, S. Enhanced Hydrogen Evolution Catalysis from Chemically...
Exfoliated 2H MoS2 Nanosheets by Sonication-Assisted Lithium

Terrones, M.; Mallouk, T. E. Fast and Efficient Preparation of

Functionalization of MoS2 Nanosheets by an Organosulfur Reaction.

Silva, C. M. P.; Leite, E. R. Single-Step Exfoliation and Covalent

Intercalation and Infrared Laser-Induced 1T to 2H Phase Reversion.

Nano Lett. 2015, 15, 6777–6784.

Liu, W.; Yang, X.; Zhang, Y.; Xu, M.; Chen, H. Ultra-stable two-dimensional MoS2 solution for highly efficient organic solar cells. RSC Adv. 2014, 4, 32744–32748.

Backes, C.; Berner, N. C.; Chen, X.; Lafargue, P.; LaPlace, P.; Freeley, M.; Duesberg, G. S.; Coleman, J. N.; McDonald, A. R. Functionalization of Liquid-Exfoliated Two-Dimensional 2H-MoS2. Angew. Chem., Int. Ed. 2015, 54, 2638–2642.

Anbazhagan, R.; Wang, H.-J.; Tsai, H.-C.; Jeng, R.-J. Highly concentrated MoS2 nanosheets in water achieved by thiglycolic acid as stabilizer and used as biomarkers. RSC Adv. 2014, 4, 42936–42941.

Yao, Y.; Tolentino, L.; Yang, Z.; Song, X.; Zhang, W.; Chen, Y.; Wong, C.-P. High-Concentration Aqueous Dispersions of MoS2. Adv. Funct. Mater. 2013, 23, 3577–3583.

Gonzalves, R. H.; Fiel, R.; Soares, M. R. S.; Schreiner, W. H.; Silva, C. M. P.; Leite, E. R. Single-Step Exfoliation and Covalent Functionalization of MoS2 Nanosheets by an Organosulfur Reaction. Chem. – Eur. J. 2015, 21, 15583–15588.

Knirsch, K. C.; Berner, N. C.; Nerd, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, L.; Vecera, P.; Halik, M.; Sanvito, S.; Duesberg, G. S.; Nicolosi, V.; Hauke, F.; Hirsch, A.; Coleman, J. N.; Backes, C. Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulide by Diazonium Salts. ACS Nano 2015, 9, 6018–6030.

Voiry, D.; Goswami, A.; Kapperla, R.; de Silva, C. C. C.; Kaplan, D.; Fujita, T.; Chen, M. W.; Asefa, T.; Chhowalla, M. Covalent functionalization of monolayered transition metal dichalcogenides by phase engineering. Nat. Chem. 2015, 7, 45–49.

Tsang, Z.; Wei, Q.; Guo, B. A generic solvent exchange method to disperse MoS2 in organic solvents to ease the solution process. Chem. Commun. 2014, 50, 3934–3937.

Sim, D. M.; Kim, M.; Yim, S.; Choi, M.-J.; Choi, J.; Yoo, S.; Jung, Y. S. Controlled Doping of Vacancy-Containing Few-Layer MoS2 via Highly Stable Thiol-Based Molecular Chemisorption. ACS Nano 2015, 9, 12115–12123.

Yamamoto, M.; Einstein, T. L.; Fuhrer, M. S.; Cullen, W. G. Anisotropic Etching of Atkinomially Thin MoS2. J. Phys. Chem. C 2013, 117, 25643–25649.

Wu, J.; Li, H.; Yin, Z.; Li, H.; Liu, J.; Cao, X.; Zhang, Q.; Zhang, H. Layer Thinning and Etching of Mechanically Exfolitated MoS2 Nanosheets by Thermal Annealing in Air. Small 2013, 9, 3314–3319.

Nan, H.; Wang, Z.; Wang, W.; Liang, Z.; Lu, Y.; Chen, Q.; He, D.; Tan, P.; Miao, F.; Wang, X.; Wang, J.; Ni, Z. Strong Photoluminescence Enhancement of MoS2 through Defect Engineering and Oxygen Bonding. ACS Nano 2014, 8, 5738–5745.

Liu, W.; Yang, X.; Zhang, Y.; Xu, M.; Chen, H. Ultra-stable two-dimensional MoS2 solution for highly efficient organic solar cells. RSC Adv. 2014, 4, 32744–32748.

Backes, C.; Berner, N. C.; Chen, X.; Lafargue, P.; LaPlace, P.; Freeley, M.; Duesberg, G. S.; Coleman, J. N.; McDonald, A. R. Functionalization of Liquid-Exfoliated Two-Dimensional 2H-MoS2. Angew. Chem., Int. Ed. 2015, 54, 2638–2642.

Anbazhagan, R.; Wang, H.-J.; Tsai, H.-C.; Jeng, R.-J. Highly concentrated MoS2 nanosheets in water achieved by thiglycolic acid as stabilizer and used as biomarkers. RSC Adv. 2014, 4, 42936–42941.

Yao, Y.; Tolentino, L.; Yang, Z.; Song, X.; Zhang, W.; Chen, Y.; Wong, C.-P. High-Concentration Aqueous Dispersions of MoS2. Adv. Funct. Mater. 2013, 23, 3577–3583.

Gonzalves, R. H.; Fiel, R.; Soares, M. R. S.; Schreiner, W. H.; Silva, C. M. P.; Leite, E. R. Single-Step Exfoliation and Covalent Functionalization of MoS2 Nanosheets by an Organosulfur Reaction. Chem. – Eur. J. 2015, 21, 15583–15588.

Knirsch, K. C.; Berner, N. C.; Nerd, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, L.; Vecera, P.; Halik, M.; Sanvito, S.; Duesberg, G. S.; Nicolosi, V.; Hauke, F.; Hirsch, A.; Coleman, J. N.; Backes, C. Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulide by Diazonium Salts. ACS Nano 2015, 9, 6018–6030.

Voiry, D.; Goswami, A.; Kapperla, R.; de Silva, C. C. C.; Kaplan, D.; Fujita, T.; Chen, M. W.; Asefa, T.; Chhowalla, M. Covalent functionalization of monolayered transition metal dichalcogenides by phase engineering. Nat. Chem. 2015, 7, 45–49.

Tsang, Z.; Wei, Q.; Guo, B. A generic solvent exchange method to disperse MoS2 in organic solvents to ease the solution process. Chem. Commun. 2014, 50, 3934–3937.

Sim, D. M.; Kim, M.; Yim, S.; Choi, M.-J.; Choi, J.; Yoo, S.; Jung, Y. S. Controlled Doping of Vacancy-Containing Few-Layer MoS2 via Highly Stable Thiol-Based Molecular Chemisorption. ACS Nano 2015, 9, 12115–12123.

Yamamoto, M.; Einstein, T. L.; Fuhrer, M. S.; Cullen, W. G. Anisotropic Etching of Atkinomially Thin MoS2. J. Phys. Chem. C 2013, 117, 25643–25649.

Wu, J.; Li, H.; Yin, Z.; Li, H.; Liu, J.; Cao, X.; Zhang, Q.; Zhang, H. Layer Thinning and Etching of Mechanically Exfoliated MoS2 Nanosheets by Thermal Annealing in Air. Small 2013, 9, 3314–3319.

Nan, H.; Wang, Z.; Wang, W.; Liang, Z.; Lu, Y.; Chen, Q.; He, D.; Tan, P.; Miao, F.; Wang, X.; Wang, J.; Ni, Z. Strong Photoluminescence Enhancement of MoS2 through Defect Engineering and Oxygen Bonding. ACS Nano 2014, 8, 5738–5745.

Kapperla, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M. Phase-engineered low-resistance contacts for ultrathin MoS2 transistors. Nat. Mater. 2014, 13, 1128–1134.

Fan, X.; Xu, P.; Zhou, D.; Sun, Y.; Li, Y. C.; Nguyen, M. A. T.; Terrones, M.; Mallouk, T. E. Fast and Efficient Preparation of Exfoliated 2H MoS2 Nanosheets by Sonication-Assisted Lithium Intercalation and Infrared Laser-Induced 1T to 2H Phase Reversion. Nano Lett. 2015, 15, 5956–5960.

Wang, L.; Xu, Z.; Wang, W.; Bai, X. Atomic Mechanism of Dynamic Electrochemical Lithiation Processes of MoS2 Nanosheets. J. Am. Chem. Soc. 2014, 136, 6693–6697.