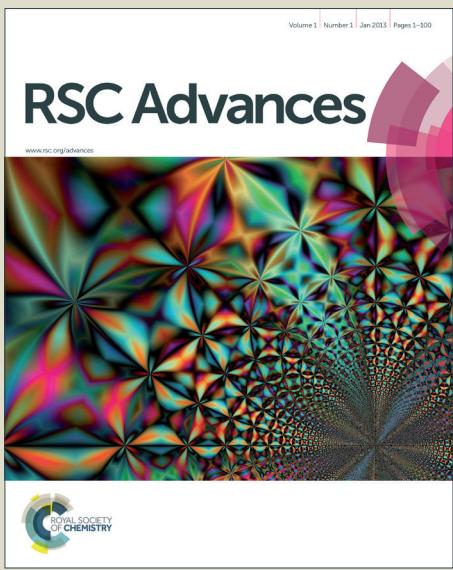
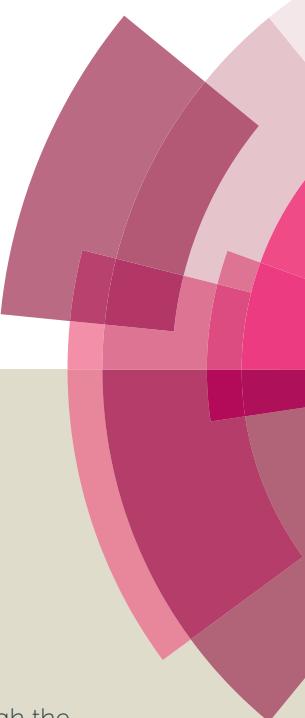


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COMMUNICATION

Ultra-Stable Two-Dimensional MoS₂ Solution for Highly Efficient Organic Solar Cells[†]

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A simple and effective procedure was developed to modify chemically exfoliated MoS₂ surfaces with a hydrophilic surfactant through electrostatic interaction. The modified ce-MoS₂ colloidal solution shows ultra long-term stability, making it a storable solution ready for highly efficient organic solar cells.

Molybdenum disulfide (MoS₂), a two-dimensional (2D) transition metal dichalcogenide (TMD)¹ consisting of hexagonal sheets of molybdenum (Mo) sandwiched between two hexagonal sheets of sulfur (S), has recently attracted enormous attention due to its novel electronic,^{2–4} optical,^{5–7} optoelectronic,⁸ and catalytic^{9,10} properties. These unique properties attract great interest in various applications including organic solar cells,^{11–15} photodetectors,^{16,17} lithium ion batteries,^{18–20} flexible logic circuits,^{21,22} and sensors.^{23,24} For instance, we have recently shown that an ultrathin layer of 2D MoS₂ sheets can serve as an efficient hole transport layer for organic solar cells (OSCs). We demonstrated that OSCs with an ultrathin layer of MoS₂ as HTL could achieve a comparable efficiency with that of commonly used HTL of poly (3, 4-ethylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS).²⁵ To promote its applications, a method for scalable synthesis of 2D MoS₂ sheets must be developed. Among various exfoliation methods to synthesize single-layer MoS₂, chemical exfoliation using lithium intercalation is the most common solution strategy to obtain single-layer MoS₂ nanosheets with scalable quantities.^{26,27} In this method, lithium is inserted between MoS₂ layers and reacts with water to produce hydrogen gas at the interface. This, in combination with ultrasonication, enables the high yield production of water dispersible chemically exfoliated MoS₂ (ce-MoS₂) sheets. However, as a general feature of solutions of 2D layered materials such as graphene, the ce-MoS₂ sheets tend to irreversibly precipitate in solutions due to restacking within a short storage period of time.^{28–30} Consequentially, the precipitation seriously affects its use during spin-coating or roll-to-roll solution processes and makes us unable to fully exploit the 2D properties of MoS₂ sheets for device applications.

Surface modification^{31–36} is one of the promising strategies to improve the solution stability of chemically exfoliated 2D materials such as graphene colloidal suspension. The ce-MoS₂ surface could be straightly decorated through the thiol ligand to the S defects.²⁶

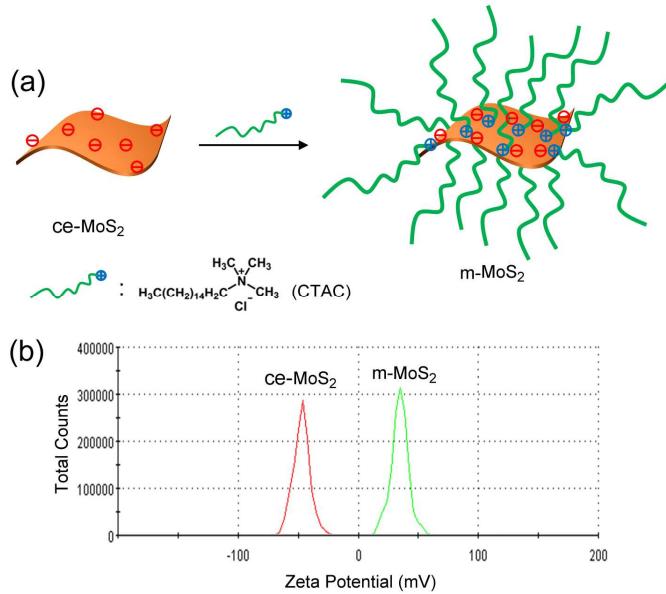


Figure 1. (a) Schematic illustration of surface modification of ce-MoS₂ by using CTAC molecules. (b) Zeta potential of ce-MoS₂ and m-MoS₂ dispersed in water.

Even though a few initial efforts have been made to modify ce-MoS₂ surfaces with polymer surfactant,³⁷ the long-term stability of modified ce-MoS₂ solution have not been systematically investigated and their applications for devices have not been reported. More importantly, due to the insulating property of the used surfactants, their influence on optoelectronic properties remains unknown. Herein, we report solution of 2D ce-MoS₂ sheets with very long-term stability suitable for high-performance solar cells fabrication. We develop a simple self-assembly procedure to modify ce-MoS₂

surfaces with a hydrophilic surfactant through electrostatic interaction. The modified ce-MoS₂ (m-MoS₂) colloidal solution shows ultra long-term stability up to our assessment of 100 days, making it a storable ink ready for optoelectronic device fabrication. This is evidenced by utilizing m-MoS₂ as a hole transport layer (HTL) for OSCs based on poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]](PTB7):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) blend as the active layer. We achieve a high efficiency of about 7.26% with negligible change of the OSCs fabricated with the m-MoS₂ solutions stored for different periods of time as an HTL. This high colloidal stability and functionality of m-MoS₂ solution pave the way towards practical device applications of these 2D atomically layered materials.

The detailed synthesis and characterization of ce-MoS₂ sheets can be found in our previous reports²⁵ and Supporting Information (Figure S1). Although the ce-MoS₂ sheets are ready to be dispersed in deionized (DI) water as a colloid solution, the sheets are easily aggregated within a short storage time, say about 3 days in our case as shown below. Since the surface of the as-prepared ce-MoS₂ sheets dispersed in DI water is negatively charged as indicated by the zeta-potential in Figure 1b, we modify the ce-MoS₂ sheets with positively charged hexadecyltrimethylammonium chloride (CTAC) via a simple self-assembly procedure through electrostatic interaction to solve the aggregation issue. As shown in Figure 1a, interaction between the positively charged CTAC molecules and the negatively charged ce-MoS₂ sheets could lead to formation of CTAC modified ce-MoS₂ hybrid sheets (m-MoS₂). We added CTAC aqueous solution into the DI water dispersion of ce-MoS₂ sheets, and then the mixture was shaken for 10 min. The resultant mixture was finally purified through high-speed centrifugation and re-dispersion. Dynamic light scattering (DLS) results in Figure 1b show that after the modification the zeta-potential of the solution of m-MoS₂ sheets became +34.7 mV from a negative zeta-potential (-47.2 mV) of the solution of ce-MoS₂ sheets. The change of zeta-potential indicates we may successfully modify the surfaces of ce-MoS₂ sheets and a good colloidal stability of the m-MoS₂ sheets may be achieved. To confirm the surface modification, X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical components before and after the modification. As shown in Figure 2, the core level peaks of Mo3d, S2s, and S2p of the m-MoS₂ sheets localized at the same binding energy positions as the non-modified ce-MoS₂. This suggests that the stoichiometric structure and phase compositions²⁵ for the ce-MoS₂ mostly remained unchanged after the modification. The appearance of N1s peak at ~395 eV, originated from N atoms in CTAC molecules, suggests that CTAC molecules were self-assembled at the surface of the ce-MoS₂ sheets.

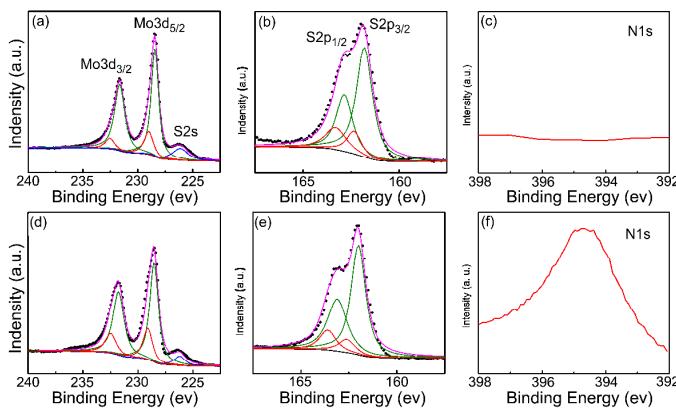


Figure 2. XPS spectra showing Mo3d, S2s, S2p, and N1s core level peaks of ce-MoS₂ (a, b, c) and m-MoS₂ (d, e, f). After Shirley background subtraction, the Mo3d and S2p peaks were deconvoluted to show the 2H and 1T phases,²⁵ represented by red and green plots, respectively.

We characterized the morphology of m-MoS₂ sheets by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figure 3b, the m-MoS₂ maintains the 2D shape and the sheets are separated from each other, suggesting high dispersibility of the m-MoS₂ sheets in the solution. Compared to the typical thickness (about 1.5 nm) of ce-MoS₂ sheets (Figure 3a), the thickness of m-MoS₂ is about 3.5 nm. The increased thickness (about 2 nm) is due to the assembled CTAC molecules at both surfaces of the ce-MoS₂ sheets (Figure 1a), which further supports the successful modification of the ce-MoS₂ surfaces. This thickness increase is also reflected by TEM observation (Figure 3c and 3d), in which the marked contrast in m-MoS₂ indicates a thicker sheet after the surface modification. Despite the obvious morphological changes, the m-MoS₂ sheets present the same XRD patterns as the ce-MoS₂ sheets (Figure 3e), which together with XPS results indicates that this electrostatic modification did not seriously affect the MoS₂ crystalline structures.

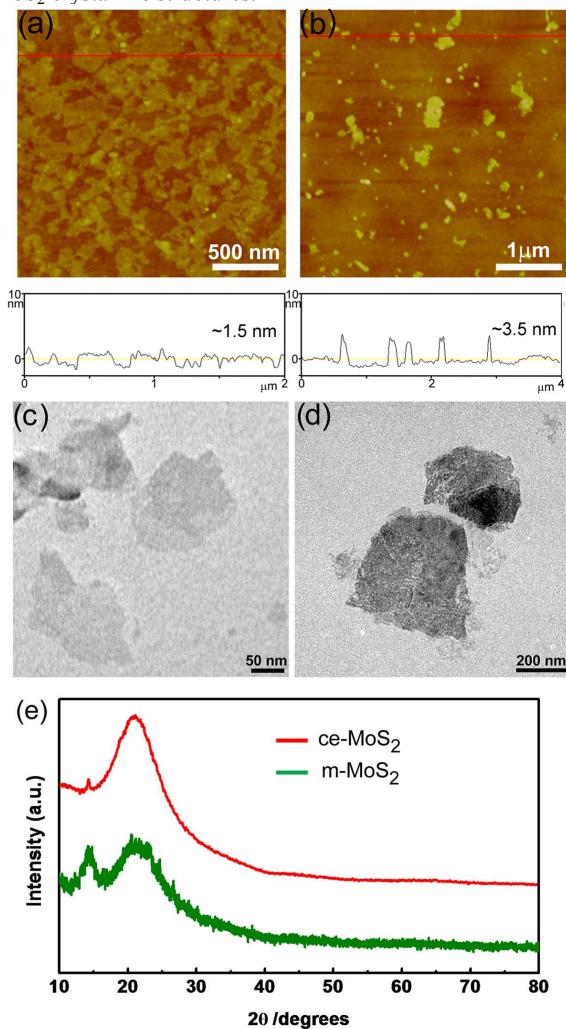


Figure 3. (a, b) Typical AFM images of ce-MoS₂ and m-MoS₂ sheets. (c, d) Typical TEM images of ce-MoS₂ and m-MoS₂ sheets. (e) XRD patterns for ce-MoS₂ and m-MoS₂ sheets.

To further investigate stability of the m-MoS₂ solution, we monitored the absorption coefficient at the peak position of single-layer MoS₂, *i.e.*, 672 nm, of both ce-MoS₂ and m-MoS₂ solutions (Figure 4a). We found that the absorption coefficient (after background subtraction)⁴⁰ of the ce-MoS₂ solution drastically dropped with the storage time. In contrast, the absorption coefficient of the m-MoS₂ solution remained about 99% of the original value even after 100 days storage, suggesting an excellent long-term colloidal stability. We can also directly observe formation of clusters of the ce-MoS₂ sheets in the solutions with storage time. Figure 4b presents the corresponding photographs of solutions of the ce-MoS₂ and the m-MoS₂ sheets stored for different periods of time. In the case of the solution of the ce-MoS₂ sheets, black clusters appeared after the ce-MoS₂ dispersion had been stored for only 3 days (Figure 4b-2), and after one week precipitation was obviously formed at the bottom of the bottle due to the irreversible aggregation of the ce-MoS₂ sheets (Figure 4b-3 and 4b-4). The observation is similar to the previous reports,^{26,29,38} that is, the pristine ce-MoS₂ owns a poor stability due to the aggregation of the ce-MoS₂ sheets. We believe the electrostatic repulsive-force among the CTAC molecules decorated at the ce-MoS₂ surfaces may efficiently depress restacking of the ce-MoS₂ sheets and the extension of the alkyl chains of the CTAC molecules away from the ce-MoS₂ surfaces may prevent approaching of the individual ce-MoS₂ sheets. As a result, the improved colloidal stability is most likely to be originated from both the electrostatic repulsion and the steric hindrance effect of CTAC molecules at the ce-MoS₂ surfaces.

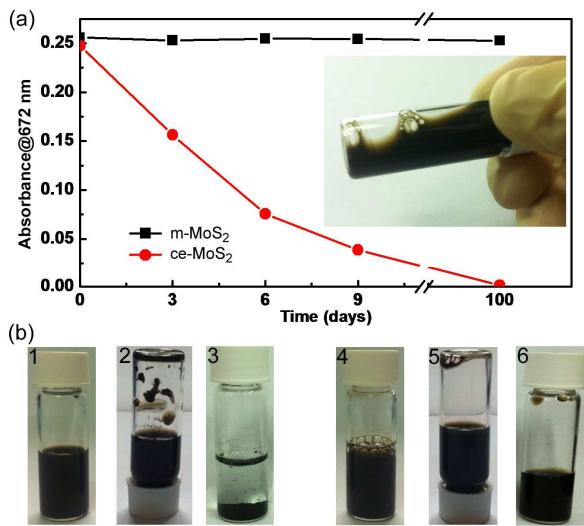


Figure 4. (a) The normalized absorbance coefficient of solutions of ce-MoS₂ and m-MoS₂ at 672 nm as a function of storage time. The inset is the photograph of m-MoS₂ colloidal ink stored for 100 days. (b) Photographs (1, 2, 3) of ce-MoS₂ and (4,5,6) of m-MoS₂ colloidal solutions stored for 0 day (1, 4), 3 days (2, 5), and 9 days (3, 6), respectively.

To evaluate the suitability of m-MoS₂ as a storable solution for optoelectronic applications, we fabricated OSCs by using the MoS₂-based materials as HTL,²⁵ including the freshly prepared solutions and the ones stored for different periods of time. As shown in Figure 5a, our OSCs compose of an ultrathin film of ce-MoS₂ or m-MoS₂ inserted between the ITO anode and the active layer of PTB7:PC₇₁BM. A dense HTL with good coverage was obtained through 3-time spin-coating from the MoS₂-based solutions. The current density-voltage (*J*-*V*) curves are shown in Figure 5b and the

performance data are summarized in Table 1. The device based on the freshly prepared m-MoS₂ solution has a PCE of 7.26% with J_{sc} of 14.71 mA cm⁻², V_{oc} of 0.73 V, and FF of 0.676. This efficiency is comparable with that of the control device based on the freshly prepared ce-MoS₂ solution, which has a PCE of 7.12% with J_{sc} of 14.63 mA cm⁻², V_{oc} of 0.73 V, and FF of 0.667. The external quantum efficiency (EQE) spectra for devices with the freshly prepared ce-MoS₂ and the m-MoS₂ solutions are shown in Figure 5c, suggesting nearly the same photocurrent of the devices. As a result, we show that a CTAC insulating modification layer at the ce-MoS₂ sheet surfaces do not change the hole transport functionality of m-MoS₂. Most importantly, by utilizing the m-MoS₂ solution after 3-day storage, the device performance has negligible change (PCE=7.14%), while the PCE of the device with an HTL layer fabricated by using the ce-MoS₂ solution after 3-day storage decreases to 5.35%. The performance deterioration of the device involved the ce-MoS₂ sheets is believed to be caused by the ce-MoS₂ precipitation. The PCE as a function with the storage time of both ce-MoS₂ and m-MoS₂ solutions used for the HTL fabrication are summarized in Figure 5d. Because complete precipitation of the ce-MoS₂ happened after 6-day storage, we gave up device fabrication by using these totally precipitated ce-MoS₂ samples. We notice that, the PCE of the OSCs with the m-MoS₂ as HTL shows little change even if the m-MoS₂ solution with 100-day storage is used for device fabrication (Table 1 and Figure S2). The results suggest that our surface modification can not only significantly enhance the long-term dispersibility of ce-MoS₂ sheets, but also the modification do not influence the device performance. The excellent colloidal stability of our m-MoS₂ solution makes it a promising storable ink with compatibility for solution-based optoelectronic applications.

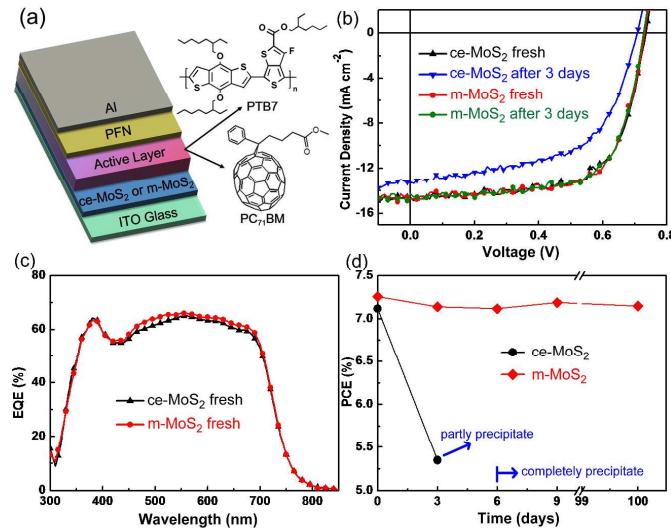


Figure 5. (a) Chemical structures of PTB7 and PC₇₁BM and schematic of the OSCs architecture: ITO/ce-MoS₂ or m-MoS₂/PTB7:PC₇₁BM/PFN/Al. (b) *J*-*V* curves of devices fabricated by using different MoS₂ solutions with various storage times. (c) Corresponding EQE spectra for devices with freshly prepared ce-MoS₂ and m-MoS₂ solutions. (d) PCE change of the devices fabricated by using ce-MoS₂ or m-MoS₂ solutions with various periods of time.

In summary, we developed highly stable solution of ce-MoS₂ sheets via a simple surface surfactant self-assembly through electrostatic interaction. As compared to the poor stability of the solution of ce-MoS₂ sheets, our CTAC modified m-MoS₂ colloidal

solution showed ultra long-term stability without change up to 100-day, which is mainly attributed to the electrostatic repulsion and the steric hindrance effect of CTAC molecules at the ce-MoS₂ surfaces. The long-term stability of the dispersion of m-MoS₂ sheets makes it a storable ink for optoelectronic applications. The performance of OSCs based on the m-MoS₂ as HTL exhibits negligible change after the m-MoS₂ solution was stored for 100 days. This high colloidal stability and functionality of m-MoS₂ ink open a venue for the emerging 2D materials and scalable optoelectronic applications with low-cost solution-processable procedures.

Table 1. Device performance under AM 1.5G illumination (100 mWcm⁻²) of OSCs fabricated with ce-MoS₂ or m-MoS₂ solutions with various storage times.

HTL in Devices	Voc [V]	Jsc [mA/cm ²]	FF	PCE [%]
ce-MoS ₂ (fresh)	0.73	14.63	0.667	7.12
ce-MoS ₂ (after 3 days)	0.71	13.27	0.568	5.35
m-MoS ₂ (fresh)	0.73	14.71	0.676	7.26
m-MoS ₂ (after 3 days)	0.73	14.29	0.684	7.14
m-MoS ₂ (after 6 days)	0.73	14.90	0.655	7.12
m-MoS ₂ (after 9 days)	0.73	14.35	0.686	7.19
m-MoS ₂ (after 100 days)	0.73	14.56	0.673	7.15

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental Section, STEM image, XRD pattern]. See DOI: 10.1039/c000000x/

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A simple self-assembly procedure was developed for preparing solution of 2D exfoliated MoS₂ sheets with very long-term stability suitable for high-performance solar cells fabrication.

