Conductive Paintable 2D Layered MoS\textsubscript{2} Inks

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Conductive and paintable inks of 2D layered MoS\textsubscript{2} with aspect ratio-dependent conductivity are demonstrated. Using ultrasonically assisted solvent-exfoliation of MoS\textsubscript{2}, 2D and few-layer suspensions become inks that provide smooth films when painted. Conductivity of painted 2D MoS\textsubscript{2} inks can be modulated by length and width, where the aspect ratio dependence of conductivity is linked to the painting direction. Inks of solvent-exfoliated MoS\textsubscript{2} can be painted as conductive films without polymeric additives.

Research on two-dimensional (2D) layered materials such as graphene\textsuperscript{(1)}, transition metal dichalcogenides (TMDs), carbide and carbonitride relatives called MXenes\textsuperscript{(2)} has progressed beyond discovery to myriad applications.\textsuperscript{(3-5)} In all applications where electronic transport is important, 2D materials\textsuperscript{(6)}, their assemblies, deposition, homo- and hetero-interfaces\textsuperscript{(7, 8)}, layered networks, and composite with polymers\textsuperscript{(9)}, strongly influence the nature of conductivity and consequently, the type of electrode or device. Photonics and optoelectronic investigations\textsuperscript{(10)} are also sensitive to engineering of 2D materials and their composites.\textsuperscript{(11)}

Of the TMD class of 2D materials, MoS\textsubscript{2} remains popular, relatively easy to prepare, relatively chemically stable. It is a classic layered material\textsuperscript{(12)} and solid-state lubricant in its bulk form. It has been examined extensively in 2D electronic and optoelectronics\textsuperscript{(13-16)} due to the relative ease in many exfoliation methods. It can also be grown using physical and vapor deposition as single molecular layers on various substrates, and more recently by
electrochemical methods.(17)

Exfoliation of parent bulk crystals to give 2D and few-layer MoS$_2$ dispersions in solvents may also be promising functional inks of various types. Whether thixotropic or dilatant, inks from particle dispersions are the basis of many printing and coating technologies. Incorporating new functionality using 2D materials with standard processing has potential for interesting applications. (18)

Inspired by MoS$_2$ used in semi-fluid thixotropic lubricants, we developed a 2D material paint without using polymer additives. Using ultrasonically assisted solvent exfoliation, which is useful for high-through and high quality dispersions of graphene and a range of TMDs.(4, 5, 19, 20), conductive MoS$_2$ paints are reported here.

Modulating the electrical properties of MoS$_2$ and many assemblies or networks of deposited TMD flakes is sensitive to the method of deposition and growth method of the 2D materials. Conductive polymer additives can hide underlying properties by adding sheet-to-sheet grain boundary and contact resistance, and this is important for paintable inks of 2D materials that may display conductivity that is dependent on a coating method for example(21).

Here, we developed inks using high concentrations of exfoliated MoS$_2$ 2D layer suspensions that can be painted as uniform films on substrates. Conductivity is controlled at material-level by high quality exfoliated 2D sheets. Painted MoS$_2$ in-plane electronic conductivity is altered by the painting direction and aspect ratio of coated films. This 2D material paint and insights into the correlation between paint application has scope for diverse application requiring TMD and layers of 2D materials as a cohesive and conductive thin film that can be painted or sheer thinned into uniform layers or as more complex structure.

**Experimental**

MoS$_2$ powder with as-received average particle size < 2µm (Aldrich) was used as received. MoS$_2$ was subsequently exfoliated in solvent using ultrasonication into 2D and few-layer MoS$_2$. To create inks, we followed a procedure like our work on 2D Bi$_2$Te$_3$. (21) A
mass of 0.5 g of MoS$_2$ was sonicated in 1 mL of 1-cyclohexenyl pyrrolidine (CHP) solvent for 800 mins. The 2D MoS$_2$ suspension was then centrifuged at 4500 rpm for 45 min. For each dispersion, the supernatant was removed and the mixture (ink) was then painted onto substrates (glass, Si and SiO$_2$) using an artist brush. The material was distributed evenly across the glass slides in several aspect ratios (width, length) to constant thickness of ~4 µm. The substrates were then annealed at 100 °C for 3 h. Physical characterization was carried out using scanning electron microscopy (SEM) using a Hitachi S4800, transmission electron microscopy (TEM) at 200 kV using a JEOL 2100F, Raman scattering spectroscopy, and electrical transport measurements using a Keithley 2612B SourceMeter and a probe station.

Results and Discussion

Painted, conductive 2D layered MoS$_2$ films with different aspect ratio ($L \times W$) are shown in Fig. 1(a), shown schematically in Fig. 1(b). Using SEM, the morphology of the paint is shown in Fig. 1(c) and we note a relatively smooth, coherent deposition that does not contain voids or holes during painting or after drying. These films contain only exfoliated MoS$_2$, no polymer or conductive additives to modify viscosity or conductivity. In Fig. 2, we show single 2D MoS$_2$ (a,b) and few-layered MoS$_2$ (c,d) morphology after solvent exfoliation. Widening of the van der Waals spacing from solvent intercalation and buckling are consistently observed for few-layer MoS$_2$. Raman scattering spectra confirm high quality MoS$_2$ post exfoliation and (Fig. 2(e)), and MoS$_2$ 2D sheets exhibit an expected shift in optical phonon modes, and the higher frequency $E_{2u}^1$ phonon compared to bulk MoS$_2$. Normally, Coulombic interactions between adjacent layers cause Davydov splitting that defines the frequency difference between the $(E_{2u}^1, E_{1g}^1)$ conjugate pair. The $E_{2u}^1$ mode represents sulfur atoms on adjacent layers moving in phase and exfoliation appears to modify terminating sulfur bonds that alter this mode. The ratio of $E_{1g}^1$ to $A_{1g}$ remains relatively unchanged, in agreement with the layered structure we see by TEM.

We investigated the painting of the MoS$_2$ inks onto glass substrates that were cleaned by UV-ozone treatment. Two-probe transport using In-Ga eutectic ohmic contacts across various painted strips from the MoS$_2$ ink with various aspect ratio are show in in Figure 3. Ohmic response is found in all cases, and roughly doubles in conductivity as the length is halved...
The seemingly simplistic ohmic behavior appears to follow a length-dependent resistivity interpretation, but tortuosity and complex minimum conductance paths are likely formed when the width is increased. The average in-plane conductivity is \( \sim 1.2 - 1.6 \times 10^{-5} \, \text{S cm}^{-1} \) for these 2D MoS\(_2\) painted films, analysed along the direction of painting. As the aspect ratio is reduced to a square (equal length and width), the lateral 2D and few-layer sheet-to-sheet contacts provide alternative conduction paths between MoS\(_2\) or likely around scattering centres. The absolute conductance of wider films is evidently lower than for narrower ones (Fig. 4(a)), the conductivity slightly reduces to \( 1.5 \times 10^{-5} \, \text{S cm}^{-1} \). A similar relative trend holds as a function of overall painted film area (Fig 4(b). When we analyse this using a linear trend, the conductivity varies as \( 2.8 \times 10^{-5} \, \text{S cm}^{-1} \cdot \text{cm}^{-1} \ (L \times W) \). Thus, widening the 2D MoS\(_2\) paint provide conductance paths that improve overall conductivity measured along the length \( (L) \). This is confirmed in Fig. 4(c), where we find that lower aspect ratios \( (L/W) \) provide more conductive films using 2D MoS\(_2\) analyzed along the painted direction. As aspect ratio is dimensionless, the conductance is higher for any aspect ratio when the width (parallel to source-drain) is narrower. This behavior may be particular to layered materials whose shear-thinning during painting controls in-plane electronic conductivity. Other deposition methods might also impart a directional conductivity dependence(22). Wider films introduce tortuosity to the grain boundary resistivity for given thickness, and the nature of the grain-boundary contacts influence conductivity. Fundamental transport models for materials with either small or high bandgaps may explain conductivity with 3D vs 2D reduced dimensionality, and future studies underway will address some general queries in painted films or assemblies with random sheet-to-sheet contacts: does the density of contacts between 2D sheets (for a given thickness) control overall conductivity? Is the lowest resistance path a function of preferred directionality of 2D sheets? Conductivity measured along the width \( (W) \) is similarly modified by variation of the length \( (L) \), and so can anisotropy in 2D material deposition, variation in 2D sheet anisotropy or thickness(23), affect the global anisotropy in conductivity for different painted films of 2D materials we show here? For any functional, complex shaped films, electrodes or related where the 2D material is printed, painted, sprayed or deposited in a manner that adds ‘texture’ to the material’s nanostructure, or preferential orientation of 2D and few-layer sheets, the dependence of
conductivity on film aspect ratio is intrinsically important.

Conclusions

Smooth, paintable films from 2D MoS$_2$ ink are possible using solvent exfoliation without polymer additives. Electrical conductivity is enhanced by depositing narrower films at most aspect ratios, or shorter films at fixed width. Future work is necessary to understand the fundamental basis for reduced conductivity in wider painted films of equal length, and the prospects of paintable 2D materials in applications where electronic conductivity modification is important. The ability to paint arbitrary coatings provides a method for printable electronics, complex patterned catalytic, electrochemical or other coatings/electrodes on a wide range of substrates.

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Figure 1. (a) Image of a typical painted film on a glass substrate from 2D MoS$_2$ ink. (b) Schematic representation of 2-probe measurement of painted 2D MoS$_2$ film using In-Ga eutectic ohmic contact. (c) Plan view SEM image of the top surface of the 2D MoS$_2$ ink as a painted film.
Figure 2. (a) Bright field plan-view TEM image of a single 2D MoS$_2$ flake and (b) cross-sectional TEM image of exfoliated few-layer MoS$_2$. (c) Raman scattering spectra of exfoliated 2D MoS$_2$ ink suspensions. (d) Raman scattering spectra for bulk MoS$_2$ powder and exfoliated MoS$_2$. 
Figure 3. I-V response of a set of painted films of exfoliated MoS$_2$ ink on glass, with different length and width (see insets).
Figure 4. Conductance form several painted MoS$_2$ films of various length ($L$) and width ($W$) as a function of (a) painted film length, (b) total film area, (c) aspect ratio ($L/W$). The conductance was measured along the direction of the painting direction, i.e. $L$. 