Supporting information:

2D-Molybdenum Disulfide-Derived Ion Source for Mass Spectrometry

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S1. Materials, synthesis, and characterization

a. Chemicals:

All the chemicals were purchased commercially and used directly without further purification. Bulk MoS_2 powder and 1.6 M n-butyllithium (hexane), C_{60} , C_{70} , and glucose were purchased from Sigma Aldrich. Benzoquinone, iodine (I₂), benzoic acid, and acetic acid were purchased from Rankem. All the HPLC grade solvents were purchased either from Sigma Aldrich or Rankem. Water used was Milli-Q water, having conductivity of 0.05 μ Scm⁻¹ and total organic carbon content was below 2 ppb.

b. Synthesis of MoS₂:

 $MoS_2 NSs$ were synthesized using chemical exfoliation method from bulk MoS_2 powder.¹ In a round bottom flask, 300 mg of bulk MoS_2 powder was taken in argon atmosphere as a precursor material to which 3 mL of 1.6 M n-butyllithium was added. It was then stirred for two days under the same condition at room temperature (23 °C). The product was then washed with hexane, followed by 100 mL of distilled water. This was done to remove excess reactant form the solution mixture. The final solution was agitated in a bath sonicator for 1 h. Thereafter, the aqueous dispersion was centrifuged at 18000 rpm to remove un-exfoliated MoS_2 from the mixture. Asprepared 2D-MoS₂ was further characterized with UV- Vis, Raman spectroscopy, and transmission electron microscopy.

c. Characterization of the as-synthesized 2D-MoS₂:

As-synthesized 2D-MoS₂ was first characterized using UV-vis spectroscopy. The UV-vis spectra presented at **Figure S2c** show one major peak at 415 nm and two small humps at 618 and 671 nm. TEM image confirms that the exfoliated MoS₂ are of few layers (**Figure S2a**). The lattice spacing ($d_{100} = 0.27$ nm) of (100) plane of MoS₂ is shown in **Figure S2b** and the inset of the Figure shows the FFT pattern of the same. Major characterization was done using Raman spectroscopy. **Figure S2d** shows two different Raman spectra. Bottom spectrum is for bulk MoS₂ powder, while the Raman spectrum of as-prepared MoS₂ is presented at the top. We see a large gap of 27 cm⁻¹ between E¹_{2g} and A_{1g} in the bulk spectrum, which got shrunk in exfoliated MoS₂. The gap in the top spectrum is almost 18 cm⁻¹ and this is matched with he reported literature.²

d. Fabrication of 2D-MoS₂-Coated paper:

Figure S3a schematically illustrates the overall fabrication procedure of MoS_2 -coated paper. Typically, the dispersed MoS_2 solution of 10 ml was drop casted on a Whatman 42 filter paper kept on a glass petri-dish. The filter paper was folded in such a way that during drop casting, the solution should not spill out from the paper. Subsequently, the paper was dried at 35-40 ^{0}C in a hot air oven overnight. This dried paper was used directly for further experiments. Finally, the dried paper was characterized through Raman spectroscopy and Scanning electron microscopy (SEM).

e. Characterization of the fabricated paper:

The MoS₂-coated paper was first characterized using SEM. **Figure S3b** and **c** show the difference between uncoated and coated paper. In coated paper, we observed that MoS₂ layers got stacked during deposition and drying. This was further confirmed by the Raman spectrum of the coated paper. The Raman spectrum presented at **Figure S3e** shows that the E^{1}_{2g} -A_{1g} gap got further

increased from 18 cm⁻¹ to 22-23 cm⁻¹.³ In **Figure S3d**, we have shown a Raman map of the MoS₂-coated paper. This confirms uniform coating of MoS_2 over the paper.

This paper was used for multidimensional applications such as fabrication of flow-induced energy harvesting, ion generation and alcohol sensing.

S2. Experimental setup

a. Design of the flow current device:

A custom-built setup was used for measuring flow-induced current. To build the setup, a rectangular shaped paper of 1×2 cm² area was stuck on a glass slide at its edge using a cellophane tape. Two silver contacts were made with silver paste to connect the copper wires with a picoammeter (Keithley 6485). **Figure S1d** shows the optical image of the device and inset of the Figure shows a zoomed in image of the same. Optimum contact distance was maintained by measuring the flow-induced current by varying the distance between two silver contacts (1-7 mm). We held the glass slide by a clamp which was mounted on a xyz micro positioning stage. Then we placed a fused silica capillary over the rectangular paper. The capillary was used to flow the fluids with a preferred flow rate. Flow direction and velocity were also controlled by placing an inlet of a vacuum pump in front of the paper. The pressure was controlled by a regulator and set to ~10⁻² bar. Flow rate of the solvents was maintained through a syringe pump (NE-300). The background current of the picoammeter with (**Figure S1b**) and without (**Figure S1a**) connecting to the device but before flowing any liquid. In **Figure S1e** we show a photograph of the entire setup, in which the picoammeter shows a reading of 0.24 μ A.

We have also measured the resistance across the electrode during methanol flow. The resistance comes in the range of 50 to 100 k Ω (~0.1 M Ω). This is similar to the resistance of bulk methanol. This large resistance hints that the current generation must be due to the charged species generated in the flow.

S3. Experimental details

a. Measurement of the terminal velocity of the liquid flowing over MoS₂-coated paper:

We captured a video clip during the liquid flow over MoS_2 -coated paper. Parameters of the device were fixed at a constant value, such as $U_L = 22 \ \mu l/min$, $\Theta = 45^0$, and methanol was used as a solvent. Here Θ corresponds to the angle of inclination of the MoS_2 -coated paper with respect to the horizontal plane. We measured the travel time of liquid flow through the filter paper and it was measured within 1 cm, starting from a point at one end (where the opening outlet of the fused silica capillary was placed on the paper) to the other end of the paper. Average of three consecutive measurements yields the terminal velocity of the fluid moving over MoS_2 -coated paper surface and it was 2.45 mm/s.

b. Open circuit potential measurements:

The open circuit potential was measured through an electrochemical analyzer and the data are shown in **Figure S10b**. The flow rate of methanol was set at 22μ l/min. **Figure S10d** shows the change in the potential with the viscosity of the flowing solvent.

c. Mass spectrometric measurements:

All the mass spectrometric experiments were performed in a LTQ XL mass spectrometer from Thermo Scientific. In the streaming ion source, we used methanol with a flow rate of 22 μ l/min. and flow rate for the analyte was 11 μ l/min. The ion source was held on a xyz micro positioning stage and the glass slide was fixed at an angle of 45° with horizontal plane using a clamp. The angle was measured through a protractor. We also held a USB digital camera to adjust the distance between the paper tip and the inlet of the mass spectrometer. The average size of the paper used was 50 mm². The tube lens and the capillary voltages of the mass spectrometer were set to zero to avoid ionization within the inlet region. Sheath gas flow was kept at zero psi. Data acquisition was done in a continuous mode. All the data were recorded in negative ion mode, as during the flow we always ended up with the anions flowing with the liquid. The positive mode spectra had no signal. We have compared both positive and negative mode mass spectra of C₆₀ as shown in **Figure S33**; however, we could not observe any such background signal as shown in the negative ion mode mass spectrum.

S4. Control experiments for current generation

a. Drying time-dependent experiment:

An experiment was conducted to monitor the effect of capillarity in the filter paper on current generation. We have initially run the experiment by flowing methanol with a flow rate of $22 \,\mu$ l/min and waited for 40 s to stabilize the current. After that, we have switched off the syringe pump and waited for 10 sec. This was repeated two more times. We observed that if we allow a continuous flow of liquid on a wet paper, an instantaneous increment of current can be avoided. We infer that the capillary force of the paper results in generating I_{fmax}.

b. Current measurement on MoS₂-coated glass and plastic slides:

We prepared MoS_2 -coated glass and polystyrene slides in a similar way. We made two silver contacts over these two surfaces. Flowing of methanol over these MoS_2 -coated substrates also generates the current as shown in the I_f-t trace in **Figure S6**.

c. Effect of vacuum pump on the stability of current:

We observed that placing the inlet of a vacuum pump at the end of the MoS₂-coated paper makes the flow-induced current stable. This pump increases the force, experienced by the liquid resulting in a unidirectional flow with sufficient kinetic energy to overcome the zigzag flow of liquid. **Figure S7a** shows that the current fluctuation caused by the non-uniform capillary flow of liquid inside the paper in the absence of pumping. A stable current reading was monitored with pumping (**Figure S7b**). The inset of this Figure shows the schematic diagram of the setup with a pump. Pump pressure was controlled using a regulator and an optimum distance was maintained between the edge of the paper and the inlet of the pump to avoid surface drying caused by rapid suction.

d. Paper dipped experiment:

We have conducted an experiment to show that the liquid flow over the MoS₂-coated surface is an essential factor to generate the current. To verify this conjecture, MoS₂-coated paper was directly dipped into a plastic vial containing methanol and simultaneous current was measured. We observed an initial rise of the current caused by methanol filling into the fiber network of the paper through capillary action and current reached zero as the paper became fully wetted with methanol (Figure S8).

e. Flow direction dependency:

To check the relation between the polarity of the current and flow direction, we have conducted an experiment where we allowed to flow methanol in a direction shown in the inset of **Figure S9a**. Current was recorded through a picoammeter as shown in **Figure S9a**. To check the current flow direction, polarity of the picoammeter was reversed as schematically illustrated in the inset of **Figure S9b** and we observed that the polarity of the current also got reversed.

f. Simultaneous flow of alcohols:

We conducted an experiment in which methanol, ethanol, and propanol were flown on a single paper and flow-induced current corresponding to each alcohol was recorded simultaneously. This experiment was done using three separate syringe pumps. We used three separate capillaries for each pump. During the measurement of flow-induced current, we first switched on/ off the methanol pump and consecutively other pumps were switched on/off. We observed the highest and lowest current due to the flow of methanol and propanol, respectively.

g. Flow of water-methanol mixture:

Water-methanol mixture shows different physical properties in terms of viscosity, surface tension, *etc.* than the individual liquids. From a plot of viscosity *vs.* percentage of methanol, we can understand that 50 % methanol-water mixture has the highest viscosity. We have also checked the influence of viscosity of the liquid on the current generation. For that, we have flown a mixture of methanol and water with different volume ratios ranging from 0 to 100 %. We see exactly opposite curvature for both the viscosity *vs.* current profile (**Figure S13b**). We observed that at 50% methanol-water, the current is lowest. This also proves the linear relation between viscosity and current.

h. Zeta potential measurement of MoS₂:

Zeta potential of MoS_2 was measured in solution phase with a Malvern Zetasizer Nano ZSP. As-synthesized MoS_2 in water shows a zeta potential of -41.2 mV, as shown in **Figure S15**.

i. Current generation over reduced graphene oxide (rGO)-coated paper:

To demonstrate that the dissociation-induced electrokinetic effect on other 2D surfaces, we used rGO-coated paper and allowed to flow methanol over it. We observed that rGO generates a much lower current than MoS_2 . This is because the polar Mo-S bond helps in methanol dissociation and at the same time the sulfur groups help to hold the positive charge over the surface. But such dissociation and charge holding capacity are very less in case of rGO which leads to less current production. Hence, we observed approximately 250 nA on MoS_2 whereas rGO generates only 50-60 nA (**Figure S16a**).

j. C60 drop-cast experiment:

We have also studied how C_{60} ionization was affected by the methanol flow-induced current. For this experiment, we drop-casted 10 µl of C_{60} in toluene on the paper when the methanol flow current reached a stable value. We observed a sudden fall of the current (**Figure S18**). **Figure S18a** shows a schematic diagram of the setup.

k. Mixed solvent flow experiment:

To demonstrate that current depletion during drop-cast of C_{60} solution is not due to the use of nonpolar toluene, we made toluene flow along with methanol and recorded the current simultaneously. Flow of these two solvents was controlled in two different paths. In the first case, the flow of methanol was followed by flowing toluene along with methanol. In the second case, we did the flow in the reverse order, where the flow of toluene was followed by that of the toluene-methanol mixture. In both the cases, the current generation due to the flow of methanol was unrelated to the flow of toluene.

S5: Mass spectrometric experiments

a. Paper spray and electrospray ionization of C60:

For paper spray ionization, a triangular shaped filter paper was connected with a high voltage power supply. During mass spectrometry measurements, we have drop-casted C_{60} in toluenemethanol mixture and applied -4 kV to the paper to generate electrospray plume from the tip of the paper. We observed a peak corresponding to the molecular ion peak of C_{60} . The paper spray ionization setup is schematically illustrated in **Figure S20c**. In electrospray ionization, we have observed very little intensity of the molecular ion peak of C_{60} .

b. In-situ current and mass spectrometric measurement:

For this experiment, we fabricated the electrodes on the triangularly cut MoS_2 -coated paper and a picoammeter was connected through a copper wire. Finally, we held the paper in front of the mass spectrometer inlet. Upon methanol flow, we observed a current reading in the picoammeter, whereas, upon drop-casting of C₆₀, the picoammeter reading comes back to the background level. However, at the same time, ion current in the chronogram of the mass spectrometer appeared and the corresponding mass spectrum for C₆₀ ionization was observed simultaneously.

c. Tip to inlet distance dependency and the inlet temperature dependency on ionization:

We had attached the ion source over an xyz micropositioning stage. This was to see the effect of increasing distance on the peak intensity of C_{60} . In an experiment, we observed that the maximum operating distance to detect the peak at m/z 720 was up to 5 mm, from the mass spec inlet (**Figure S35a**). We had also checked the effect of the inlet temperature. We observed exponential growth of ion intensity with increasing temperature (**Figure S35b**). We kept it at 275 0 C for all our mass spectrometric measurements.



Figure S1. Background current and optical image of the overall setup. a) Background current before connecting the picoammeter to the MoS_2 -coated paper. b) After making contacts and connecting the picoammeter to the MoS_2 -coated paper. These data were recorded before flowing any liquid over the surface. c) Optical image in which the two electrodes of the picoammeter were connected to a multimeter to show that there was no external potential applied. d) Optical image of the device. Inset shows the zoomed in area of the silver contacts. e) Optical image of the entire setup during current generation. Picoammeter displayed a reading of 0.24466 μ A in one of our experiments.



Figure S2. Characterization of exfoliated MoS_2 NSs. a) Representative TEM image of assynthesized MoS_2 nanosheets. b) HRTEM image of the MoS_2 nanosheets showing a lattice spacing of 0.27 nm. Inset shows the corresponding FFT pattern. c) UV-vis absorption spectrum of the solution. Inset shows an optical image of the solution. d) Comparative Raman spectra of bulk and nano MoS_2 . Peaks are labeled. Shift in the modes indicate the extent of exfoliation.



Figure S3. Fabrication and characterization of the MoS_2 -coated paper. a) The process of fabricating MoS_2 -coated paper, schematically. i-v are different stages during the process. b) SEM image of the Whatman 42 filter paper. c) SEM image of the MoS_2 -coated Whatman 42 filter paper. Inset shows a zoomed in image of the stacked MoS_2 nanosheets. d) Raman mapping of the coated paper. Total Raman intensity was used for imaging. e) Raman spectrum of the coated paper.



Figure S4. I_f-t traces. a) Multiple cycles of flow on/off for 126 min. b) Zoomed in view of initial rise of current to $I_{f_{max}}$, c) stabilization at a value of 60% of $I_{f_{max}}$, and d) fall of current to the background level.



Figure S5. Difference in the I_{f} -t profile in different drying time scales. a) drying time of 10 sec and b) 30-35 sec.



Figure S6. Effect of support material on current generation. Current-time trace on a) a MoS_2 coated glass surface, and b) MoS_2 -coated plastic surface. Insets of both the Figures schematically show the device arrangements. Standard biological glass slides were cut into proper dimension and coated with MoS_2 films. The plastic used was polystyrene slides and the MoS_2 film was prepared in the same way (as illustrated in Figure S3a).



Figure S7. Effect of vacuum during current generation. a) Current generation without applying vacuum. b) Current-time profile after applying vacuum in front of the device, as shown schematically in the inset.



Figure S8. MoS₂-coated paper dipping experiment. We dipped the MoS₂-coated paper inside a vial containing methanol and current was recorded with time. We observed a sudden increase and subsequent fall in current. The inset schematically represents the experimental setup.



Figure S9. Flow direction and the polarity of the current. a) Current-time trace while direction of the flow is from the positive electrode to the negative electrode. Inset represents a schematic diagram of the corresponding flow direction. b) Current-time trace while the flow direction was changed in the same setup. Inset shows the schematic diagram of the corresponding flow direction; the flow direction of the liquid and the charge carrier are indicated.



Figure S10. Open circuit potential (OCP) measurement over MoS_2 -coated paper. a) schematic diagram of the device. b) The circuit diagram of the OCP measurements. c) The potential-time trace of the OCP using methanol as a flowing liquid. d) Potential-viscosity trace representing comparative potential generation using methanol, ethanol, and propanol. Each experiment was repeated thrice independently. Data are presented as mean, and error bar shows ±SD.



Figure S11. Comparative current generation profile using methanol, ethanol and propanol. The unsteady fall and rise of current in the first and third cycles are due to omnidirectional flow of liquid in the absence of a vacuum pump (as shown earlier in Figure S7).



Figure S12. Experimental validation of the electrokinetic effect. a) Current *vs.* dielectric constant of the liquid. b) Current *vs.* viscosity of the liquid. c) Current *vs.* the ratio of dielectric constant and viscosity of the liquid. d) current *vs.* contact distance. e) Current *vs.* flow rate. f) Current *vs.* inclination angle. Appropriate fits are used. Each experiment was repeated thrice independently. Data are presented as mean, and error bar shows \pm SD.



Figure S13. Magnitude of current with dissociation constant and viscosity. a) Current- pK_a trace of all the alcohols. Each experiment was repeated thrice independently. Data are presented as mean, and error bar shows \pm SD. b) Viscosity⁴ and current profile in different concentration of methanol in water flow.



Figure S14. Mechanistic understanding of the current generation. a) Schematic representation of the speculated phenomenon, dissociation-induced electrokinetic effect. b) Different stages of the current-time trace leading to correlation of the mechanism.



Figure S15. Zeta potential (ζ) analysis of MoS₂ in solution. Zeta potential distribution shows that the maximum zeta potential of MoS₂ solution is -41.2 mV.



Figure S16. Current generation on rGO. a) Current generation on reduced graphene oxide. Inset shows the characteristic Raman features of the rGO-coated paper. b) UV-vis spectrum of rGO used for current generation. Inset presents a TEM image of the same.



Figure S17. Current-time trace of other solvents. Current generation using a) water, b) acetic acid, c) dimethyl formamide, d) acetone, e) acetonitrile, f) dichloromethane, g) chloroform, h) toluene and i) hexane. The unsteady fall and rise of current in b and c are due to omnidirectional flow of liquid in the absence of a vacuum pump (as shown earlier in Figure S7).



Figure S18. Effect of electron scavenging molecule during current generation. a) Schematic diagram of the experimental setup. b) The current-time trace during drop-casting of 10 μ l of C₆₀ while the flow is on. The flowing liquid is methanol here with 22 μ l/min flow rate.



Figure S19. Current time trace in mixed solvent flow. a) Flow of methanol first then mixture of toluene and methanol. b) Flow of toluene first then mixture of methanol and toluene.



Figure S20. Comparison of our method of ionization with standard paper spray ionization and electrospray ionization methods. a) PSI mass spectrum of C_{60} . b) ESI mass spectrum of C_{60} . We observed a very low intense peak for C_{60} . However, peaks corresponding to C_{60} dimer, methoxide, and hydroxide added C_{60} were not observed. Both the PSI and ESI MS were done in toluene-methanol mixture. c) Schematic representation of paper spray ionization in which potentials of the order of kilovolts are applied for ionization. Similar is the case for electrospray ionization. d) Comparative study between these conventional methods with our method to obtain C_{60} peak at m/z 720.



Figure S21. Comparative mass spectra of C_{60} flowing with three different alcohols. a) Methanol, b) ethanol, and c) propanol. Actual intensities of individual spectra are presented in the Y axis. d) Actual intensities of the peak m/z 720 are plotted against the viscosity of alcohols.



Figure S22. Fragmentation pattern of hydroxide and methoxide added peak of C₆₀. a) MS^1 spectrum recorded during the flow of C₆₀ along with methanol. b) MS^2 spectrum of m/z 751. It shows the loss of m/z 31 corresponding to methoxide ion. c) MS^2 spectrum of m/z 737. It shows the loss of m/z 17 corresponding to the hydroxide ion.



Figure S23. Fragmentation pattern of ethoxide and propoxide added peak of C₆₀. a) MS² spectrum of m/z 779. It shows the loss of m/z 59 corresponding to propoxide ion. b) MS² spectrum of m/z 765. It shows the loss of m/z 65 corresponding to ethoxide ion.



Figure S24. Mass spectra of C₆₀ in different solvents with varying polarity. a) Acetone, b) acetonitrile, c) dichloromethane, d) chloroform, e) toluene, and f) Dimethylformamide. A peak at m/z 764 is observed in DMF along with m/z 720 ([C₆₀]⁻) which could be due to the species [C₆₀N(CH₃)₂]⁻.



Figure S25. Glucose addition of C₆₀. a) MS^1 spectrum recorded during the flow of methanolic solution of C₆₀ and glucose. We observed a peak at m/z 899 at m/z 179 higher than the molecular ion peak of C₆₀. Inset shows the isotopic distribution of the peak. b) MS^2 spectrum of the peak at m/z 899 leads to the loss of m/z 179 corresponding to deprotonated glucose.



Figure S26. Extent of ionization of C_{60} . a) Total ion chronogram (TIC). b) Mass spectrum at maximum ion intensity and mass spectrum after reaching equilibrium.



Figure S27. *In-situ* current measurement and mass spectrometry. a) (i) Current-time trace measured using picoammeter and (ii) simultaneous ion current-time trace in the total ion chronogram. The yellow traces in both the spectra indicate flow of methanol over the paper and the green traces indicate the flow of methanol and C_{60} (in toluene) together. The label, Δt represents the time delay between the start of the C_{60} pump and observing peak in the mass spectrum. The delay is travel time of C_{60} over the surface. b) (i) Mass spectrum in the absence of C_{60} and (ii) mass spectrum during the flow of C_{60} along with methanol flow. The reduced current generation in the first cycle is due to the mechanical instability of the flow in front of the mass spectrometer inlet due to high vacuum. Once the paper gets sufficiently wet and the tip to inlet distance is optimized, it produces continuous and stable flow to give proper signal in picoammeter (second cycle) as well as in the mass spectrometer. We choose optimal tip to inlet distance after achieving a background signal as shown in b(i).



Figure S28. Mass spectra of C₇₀. a) MS^1 mass spectrum of C₇₀ during the flow of methanol. b) and c) MS^2 spectra of peaks at m/z 857 and m/z 871. We observed similar loss of m/z 17 and 31 corresponding to hydroxide and methoxide species.



Figure S29. Molecular ionization of benzoquinone and iodine. a) MS^1 spectrum of benzoquinone. The peak at m/z 108 corresponds to the molecular ion peak of benzoquinone. b) MS^1 spectrum of iodine. Any of these peaks was not present during the experiment with normal paper.



Figure S30. Detection of ion clusters. SI-MS spectra of a) tryptophan, b) hystidine and c) methylamine chloride. Deprotonated mono-, di-, tri-, and tetramer of tryptophan, mono- and dimer of histidine and di- and trimer of methylamine were observed in the mass spectrum. The experiments were done by dissolving each component in methanol at a concentration of 3 mM.



Figure S31. SI-MS of urine samples. a) MS^1 mass spectrum of uric acid during the flow of 5 µL raw urine with methanol. b) and c) $MS^2 MS^3$ spectra of peaks at m/z 167 and 124. We observed a characteristic loss of m/z 43 and 28 corresponding to loss of HCNO and CO. The inset of the Figure 32C is the MS^4 spectrum of the peak at m/z 96 which shows characteristic loss of 27 corresponding to neutral loss of HCN.



Figure S32. SI-MS of other small molecules during methanol flow. Mass spectra of a) Propanol, b) benzoic acid in acetone and c) glucose in water during the flow. Insets shows the isotopic distributions of the corresponding peaks. We have observed simultaneous current generation for propanol.



Figure S33. Mass spectra in the positive and negative ion modes. a) Positive ion mode mass spectrum of C_{60} which shows no peak. Zoomed in peaks with an absolute intensity of 0.02 are due to electronic or chemical noise in the mass spectrometer. b) Negative ion mode mass spectrum of C_{60} .



Figure S34. Interaction of ethanol vapor with the liquid flow during the course of ionization. a) Schematic representation of the setup shows the flow of C_{60} solution (in toluene) along with methanol, and the vapors of ethanol exposed to the system through a tube. b) mass spectra of C_{60} in the absence (top) and presence (bottom) of ethanol vapor. Peak indicated as m/z 765 corresponding to ethoxide added C_{60} was observed immediately upon exposure of ethanol vapor. Extracted ion chronograms of the mass selected peak at m/z 765 are plotted while the device is exposed to c) 16%, and d) 8% aqueous ethanol vapor. The rise of the chronogram indicates the presence of the ethoxide added C_{60} signal in the time window.



Figure S35. Effect of vacuum and temperature at the inlet on ionization. a) Plot of ion intensity *vs.* tip to inlet distance plot which shows that the increasing the distance leads to decreasing suction. b) Plot of ion intensity *vs.* inlet temperature. Each experiment was repeated thrice independently. Data are presented as mean, and error bar shows \pm SD.

Table S1.

Exp. No.	Exp details	Used sample	Flowing	Magnitude of current
			solvent	(n A)
1	Only air	Only air	Acetone	0
2	Blow air through 0% ethanol	Water	Acetone	2-5
	in water			
3	Blow air through 10%	Ethanol (aq)	Acetone	12-25
	ethanol in water			
4	Blow air through 20%	Ethanol (aq)	Acetone	20-40
	ethanol in water			
5	Blow air through 30%	Ethanol (aq)	Acetone	50-75
	ethanol in water			
6	Normal breath	Direct breath	Acetone	0-2
7	Breath after drinking beer	Direct breath	Acetone	6-12

A summary of various experiments using simulated breath

Appendix i

Calculation of number density (p):

We calculated an approximate number density of MoS₂ over the paper surface. To simplify our calculations, following things are assumed,

i) MoS₂ was taken as an individual molecule instead of an extended 2D layer.

- ii) Only MoS₂ exist in solution
- iii) During drop-casting the MoS₂ molecules distributed homogeneously all over the surface.
- iv) The drop-casted MoS_2 forms a monolayer of molecules.
- v) There is no loss during the drop-casting process.

Weight calculation was done by measuring the mass of MoS_2 taken before drop-casting over the paper. To measure the amount of MoS_2 drop-casted over the surface in grams, we took a similar volume of water and MoS_2 solution and then measured the weight of both. Subtracting the weight of water gives the weight of MoS_2 in the solution. For instance, we may say that the weight of MoS_2 will be in the range of μ g or 10^{-6} g in 20 ml solution. This would be $(10^{-6}/160) \times 6.023 \times 10^{23}$ molecules = 0.037×10^{17} molecules

 $N = 0.037 {\times} 10^{17}$

This many number of molecules are distributed all over the surface.

The surface area (A) of the Whatman 42 filter having a radius of 21 mm is $\prod R^2$ (1.1) A= 3.14× (21×10⁻³)² = 1323×10⁻⁶ m² = 1.3×10⁻³ m²

Hence, Number density $\rho = N/A$

$$= (0.037 \times 10^{17})/(1.3 \times 10^{-3}) \text{ m}^{-2}$$
$$= 0.028 \times 10^{20} \text{ m}^{-2} = 2.8 \times 10^{18} \text{ m}^{-2}$$

(1.2)

Appendix ii

Dipole-dipole interaction energy and the dissociation of molecules: For our calculation flow of methanol was taken as a model system

$$\Delta G^{o} = E_k + E_{dd} \tag{2.1}$$

$$E_{dd} = 1/\varepsilon_0 \left(\rho \times P_{\text{MeOH}} \times P_{\text{MoS}} \times \int_0^l r_1 dr_1 / (z^2 + r_1^2)^{3/2}\right)$$
(2.2)

For this, following are the assumptions to simplify the problem:

i) The alcohol molecules undergo dissociation at equilibrium condition

.

ii) P_{Methanol} and P_{MoS} are approximated to 1D

iii) The dipolar radius of MoS_2 is approximated to the bond distance of Mo-S bond, which is ~5.896 A^{\circ .5}

iv) The dipolar radius of R-OH molecule is approximated to the bond distance of OH bond which is ~0.956 $A^{0.6}$

v) We used free space permittivity for the calculation which is $8.8 \times 10^{-12} \text{ N}^{-1} \text{C}^2 \text{m}^{-2}$.

So, from the left-hand side of the equation,

$$\Delta G^{0} = -RTlnK_{a}$$

$$= 8.314 \text{ JK}^{-1}\text{Mol}^{-1} \times 298.15 \text{ K} \times (\text{ pK}_{a}) = 8.314 \times 298.15 \times 15.5 \text{ JMol}^{-1}$$

$$= 38.42 \times 10^{3} \text{ JMol}^{-1}$$
(2.3)

Now ΔG^0 /molecule = 38.42×10³ J/(6.023×10²³)

 $= 6.4 \times 10^{-20}$ J/molecule

Now, from the right-hand side of the equation,

$$E_k = 1/2 \text{ mv}^2$$

$$= 1/2 \ 32 \times 10^{-3} \times (2.45 \times 10^{-3})^2 \text{ J/mol} = 96.04 \times 10^{-9} \text{ J/mol}$$

$$= 96.04 \times 10^{-9} / (6.023 \text{ X } 10^{23}) \text{ J/molecule}$$

$$= 15.94 \times 10^{-32} \text{ J/molecule}$$
(2.4)

$$E_{dd} = 1/\varepsilon o \ (\rho \times P_{MeOH} \times P_{MoS} \times \int_{0}^{l} r_{1} dr_{1} / (z^{2} + r_{1}^{2})^{3/2})$$
(2.2)
$$= -1/\varepsilon o \ (\rho \times P_{MeOH} \times P_{MoS} \times \left| 1/(z^{2} + l^{2})^{\frac{1}{2}} - 1/z \right|$$
$$= \{ 1/(8.8 \times 10^{-12} \,\mathrm{N}^{-1} \mathrm{C}^{2} \mathrm{m}^{-2}) \} \{ 2.8 \times 10^{18} \mathrm{m}^{-2} \times (1 \times 3.3 \times 10^{-30} \,\mathrm{Cm})^{2} \times 10^{10} \mathrm{m}^{-1} \}$$

$$= 3.4 \times 10^{-20} \,\mathrm{Nm} = 3.4 \times 10^{-20} \,\mathrm{J}$$

This is the dipole-dipole interaction energy experienced by one methanol molecule So overall right-hand side,

= $(15.94 \times 10^{-32} + 3.4 \times 10^{-20})$ J/molecule (As the kinetic energy term is very less) Hence, by neglecting the kinetic energy we can write,

The right-hand side of the equation 1.1 results in the value of 3.4×10^{-20} J/molecule

It is thus concluded that the energy required for heterolytic bond dissociation of alcohol is comparable with the dipole-dipole interaction energy between methanol and the MoS₂ dipole.

Appendix iii

Calculation of number of ions passing across the electrode area:

For the calculation purpose we use methanol as a liquid to flow

For this calculation we assume that,

i) The number of molecules get ejected are passing through the electrodes.

ii) 100% dissociation of methanol occurs

We measured the velocity of the liquid as 2.45×10^{-3} m/s

The electrodes are separated at 1×10^{-3} m distance

Time taken for the molecules to pass the electrodes is 0.408 s.

At 0.408 s, volume of liquid ejected from the fused silica capillary is $(22 \times 10^{-6}/60) \times 0.408 \text{ l} = 0.15 \times 10^{-3} \text{ ml}.$

The density of methanol is 0.791 g/ml

So, the mass of the corresponding volume = $0.791 \times 0.15 \times 10^{-3}$ g = 0.12×10^{-3} g = $0.12 \times 10^{-3}/32$ mol

= 3.6×10^{-6} mol = $3.6 \times 10^{-6} \times 6.023 \times 10^{23}$ molecules = 22.26×10^{17} molecule = 22.26×10^{17} ions (as per the assumption)

Appendix iv

Flow rate to pump pressure conversion.

We used NE-300 syringe pump from New Era Pump Systems, Inc.

The esteemed linear force (lbf-s) can be calculated from the following equation,^{7 8}

$$F=F_m(R/R_m)$$

(4.1)

Here, F_m , R, and R_m are maximum linear force (lbf-s), rate, and maximum rate, respectively.

Now, for NE-300 model, $F_{m}\!\!=\!35$ lbs. at minimum speed, 18 lbs. at maximum speed

$$R=22 \ \mu l/min$$
$$R_m= 38 \ lbf-s$$

The pump pressure (ΔP) in psi can be calculated as below,⁸

 $\Delta P = F \times E / \{\pi D^2 / 400) / 2.45^2\}$

(4.2)

Here, E and D are the pump efficiency and the diameter of the syringe (in mm)

For a Hamilton 500 μ l gas tight syringe, D=3.11 mm.

Hence, at 90% efficiency, the pump pressure would be 2910.92 psi.

Appendix v

Mathematical validation of Helmholtz–Smoluchowski model in our system:

In Helmholtz-Smoluchowski model,

$$I_f = -\mathcal{E}\mathcal{E}_0 \zeta A_c \Delta P_r / \eta l \tag{5.1}$$

This equation is used for the streaming current across two point separated by l distance in a A_c diameter capillary.

$$\mathcal{E} = \text{Dielectric const of methanol} = 32 \text{ unit less}$$

$$\mathcal{E}_0 = \text{Free space permittivity} = 8.8 \times 10^{-12} \text{ N}^{-1} \text{C}^2 \text{m}^{-2}$$

$$\zeta = \text{zeta potential of MoS}_2 = -41.2 \times 10^{-3} \text{ V}$$

$$\eta = \text{Viscosity} = 0.5 \times 10^{-3} \text{ Nsm}^{-2}$$

$$\Delta P = 2911 \text{ psi at } 22 \text{ µl/min flow rate.}$$

$$= 2911X6894 \text{ Nm}^{-2}$$

Here we took that methanol flowing over 10 nM length MoS₂ sheets So $A_c = 10 \times 10^{-9}$ m

Now,

RHS,

$$\begin{split} \epsilon \epsilon_0 \zeta A_c \Delta P_r / \eta l &= 32 X 8.8 X 10^{-12} \times (-41.2 X 10^{-3}) \times 10 \times 10^{-9} \times 2911 \times 6894 / (0.5 X 10^{-3} \times 1 \times 10^{-3}) \\ &= 4656 \text{ nA.} \\ &= 4.656 \text{ } \mu \text{A} \end{split}$$

The maximum amount of current we achieved is $1.3 \,\mu$ A, which is quite matching with the amount of current calculated from Helmholtz-Smoluchowski model within a factor of 0.25. This loss is possibly due to the contact resistance or loss of charges by other factors.

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