

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

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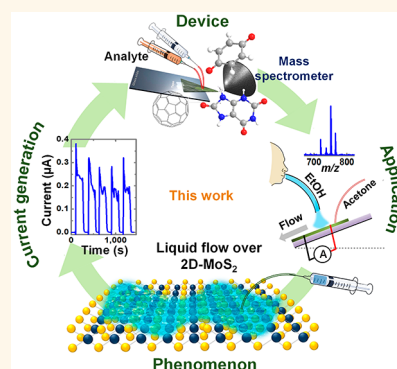
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ABSTRACT: Generation of current or potential at nanostructures using appropriate stimuli is one of the futuristic methods of energy generation. We developed an ambient soft ionization method for mass spectrometry using 2D-MoS₂, termed streaming ionization, which eliminates the use of traditional energy sources needed for ion formation. The ionic dissociation-induced electrokinetic effect at the liquid–solid interface is the reason for energy generation. We report the highest figure of merit of current generation of 1.3 A/m² by flowing protic solvents at 22 μ L/min over a 1 $\times$ 1 mm² surface coated with 2D-MoS₂, which is adequate to produce continuous ionization of an array of analytes, making mass spectrometry possible. Weakly bound ion clusters and uric acid in urine have been detected. Further, the methodology was used as a self-energized breath alcohol sensor capable of detecting 3% alcohol in the breath.

KEYWORDS: ambient soft ionization, mass spectrometry, 2D-MoS₂, dissociation-induced electrokinetic effect, ion clustering, self-energized breath alcohol sensor



Mass spectrometry has been used for a century as an analytical technique to study materials. Ionization is the primary step in mass spectrometric analysis. Several path-breaking discoveries of ionization such as electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) have revolutionized mass spectrometry in the past two decades. Yet, demand for ambient ion sources is increasingly high. Although the impact of mass spectrometry in materials has been increasing,¹ use of advanced materials for mass spectrometry is recent. Several attempts have been made to use advanced materials for easy sampling and ionization. For example, carbon nanotubes and other 1D nanostructures have made ionization possible for common analytes at an applied potential of a few volts.² Thermospray, a voltage-free ion source, was developed in the 1980s, whereby spray-based ionization was assisted by thermal energy.³ A sonic spray ionization source was developed later whereby high-speed gas flow broke up the bulk liquid to droplets, which underwent dehydration to release ionic species into the gas phase.⁴ Zero-volt paper spray was developed in 2015 whereby chromatographic paper surfaces were used to generate droplets with the help of the pneumatic force of the vacuum of the mass spectrometer.⁵ Triboelectric nanogenerators (TNGs) were also used as an alternative energy source for ionization.⁶ However, nanotechnology-enabled

molecular ionization without the application of external energy is unknown in mass spectrometry.

Deriving alternate energy on a material platform can be revolutionary.^{7–9} Sliding an aqueous electrolyte over electrically charged surfaces resulting in electrical power is such an example of energy harvesting. A considerable number of investigations on this subject have established the underlying mechanisms of current generation. For instance, generation of an electrical potential over carbon nanomaterials was discussed in a variety of pathways;^{10–18} among them, the electrokinetic effect is a celebrated mechanism.^{19,20} A macroscopic understanding of this phenomenon suggests selective ion adsorption at the liquid/solid interface resulting in the formation of an electrical double layer (EDL), composed of a diffusive layer of counterions that is separated by an electroneutral liquid layer called a Stern layer.²¹ The thickness of the diffusive layer is considered as the Debye length (λ_D). A pressure difference (ΔP) at the two ends of the stream, which is responsible for the electrokinetic effect, results in a charge separation in the

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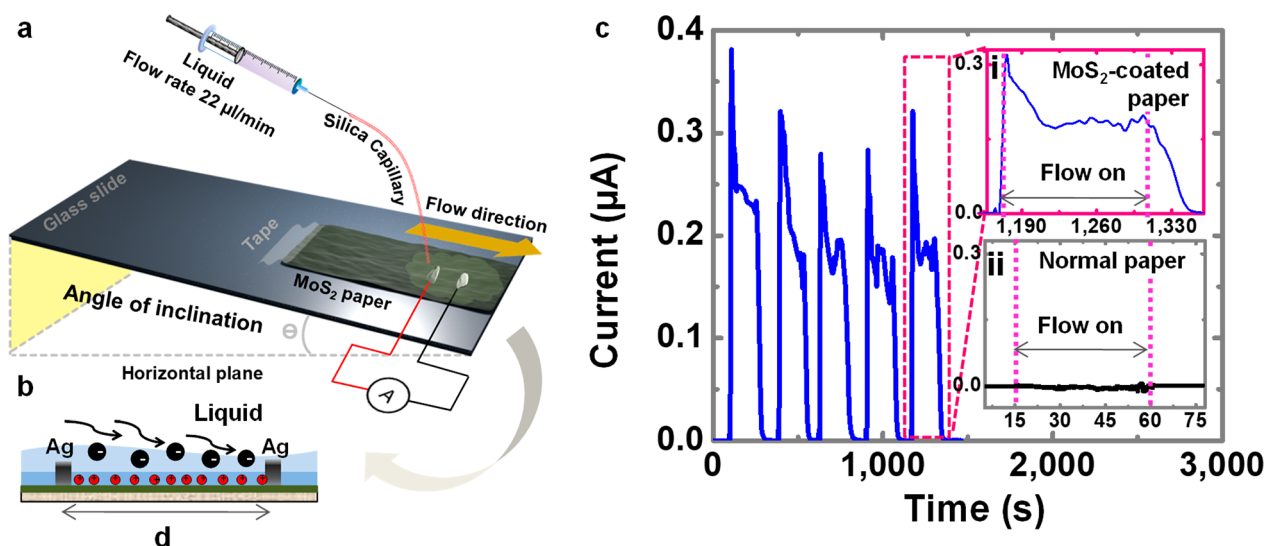


Figure 1. Liquid flow over MoS₂-coated paper in the device. (a) Schematic representation of the device fabricated for the flow-induced current or potential generation. The dark green sheet attached to the glass slide and connected to the picoammeter (A) is the 2D-MoS₂-coated paper. The device was kept inclined with an angle θ . The liquid was pushed through a syringe connected to a syringe pump (flow rate of 22 $\mu\text{L}/\text{min}$). (b) Side view of the electrode area. “d” is the contact distance. Positive and negative ions are shown as spheres. (c) Time-dependent current profile (5 repetitive on/off cycles) with methanol flow on a MoS₂ surface. Insets: (i) Zoomed-in view of one such cycle of generated current over MoS₂ and (ii) data of current generation over normal filter paper.

diffused layer, leading to a rise of the streaming potential (U_s). Pressure-induced relative motion of charged species with respect to its counterionic part in a stream is termed as streaming current (I_s). Several of the critical parameters that manipulate the magnitude and the polarity of current such as flow direction,²² surface roughness,²³ slip velocity,²⁴ charge holding, and separation capacity²⁵ have been controlled using micro- and nanostructured functional materials.

For example, hydrophobic surfaces were used to increase ion velocity. But these surfaces have large air gaps on them. Trapped air cannot hold the charge. Reduced charge-holding capacity leads to poor potential generation.^{26,27} An engineered micropatterned surface filled with oil showed enhanced voltage production.²⁸ More recently, polymer-coated carbon-based low-dimensional materials such as graphene, graphene oxide, and graphene foam drew attention for enhanced energy harvesting due to their higher ion adsorption capacity, and they generated a potential in the range of 0.4 to 30 mV.^{14,29,30} However, generated current can be shunted through such low-resistance carbon-based 2D materials due to their semimetallic characteristics.³¹ Semiconducting transition metal chalcogenides could be a better choice in this regard. Ohno *et al.* showed an output potential of over 5 V by flowing highly concentrated NaCl (1 M) droplets over single-layer MoS₂ created over a polymer substrate.³¹ Generation of current has also been observed under a potential bias; for example, 3D graphene foam over a porous nickel surface produced a 25 μA current at a bias voltage of 80 μV , having an 80 cm/s fluid velocity.³² In the past, Subramanian *et al.* reported a transverse electrokinetic effect by flowing polar liquids across an assembly of gold nanoparticles.^{33,34} However, lack of suitable materials restricts us from utilizing an electrokinetic effect for applications of societal relevance. Therefore, it is indeed necessary to study advanced materials to generate stable, repeatable, and larger currents, which can result in a cost-effective technology.

In this article, we report the flow of organic liquids over 2D-MoS₂ coated on a filter paper, and the flow of dissociated ions was utilized to generate a DC current or potential. We fabricated a small device to control the magnitude and polarity of the current. Using this technology, we report an electrokinetic current/potential-driven ambient ion source for mass spectrometry, termed “streaming ionization mass spectrometry (SI-MS)”, which is capable of imparting soft ionization of analytes without an external power supply. We demonstrated molecular ionization of fullerenes, benzoquinone, iodine, glucose, *etc.*, and mass spectra of some of their loosely bound ionic clusters were detected. To demonstrate a socially relevant application using this method, we detected uric acid by flowing raw urine over the nanostructured surface. We have also presented the experimental results, and a mechanism was proposed for power generation and confirmed by control experiments. We observed that the flow of pure methanol generated a record-high current of 1.3 μA for the prepared device in comparison to other organic solvents such as ethanol, propanol, acetonitrile, and acetone. Detailed insights on the generation of current and its dependence on the physicochemical properties of different solvents have also been obtained. Additionally, we utilized the magnitude of streaming current as a probe to detect ethanol in the breath, for which we have fabricated a paper-based disposable sensor. This cost-effective device allowed us to detect down to 3% of alcohol in the breath.

RESULTS AND DISCUSSION

Design and Characterization of the Device. The construction of our flow device is schematically illustrated in Figure 1a. A detailed description of the device with the optical images and the measurement procedure are discussed in the Methods section and Figure S1. Briefly, a Whatman 42 filter paper (pore size of 2.5 μm) was used as a support material, and 2D-MoS₂ was coated on it. On top of this coated paper, two silver contacts were made at a distance of 1 mm between them,

which were finally connected to a picoammeter (Keithley, model 6485). The synthesis procedure and characterization using various spectroscopic and microscopic techniques of a few-layer MoS₂ are presented in the [Methods section](#) and in [Figure S2](#), respectively. Similarly, a schematic illustration of the detailed fabrication procedure of the MoS₂-coated paper and its characterization are also discussed in the [Methods section](#) and in [Figure S3](#), respectively. One important point to be noted is that deposition of the MoS₂ dispersion over the paper results in a few-layer stacking of sheets, which was characterized by Raman spectroscopy ([Figure S3e](#)).

We allowed the flow of different alcohols (methanol, ethanol, propanol, *etc.*) across the two silver contacts over the fabricated surface, at a given flow rate (U_L) of 22 $\mu\text{L}/\text{min}$, and the current (I_f) was measured as a function of flow time. The data are shown in [Figure 1c](#). The flow on and off periods were within 2–3 min. [Figure 1c](#) quantifies the magnitude and the polarity of the current produced after switching on and off methanol flow for multiple cycles. A zoomed-in view of one such cycle is shown in the inset ([Figure 1ci](#)), in which methanol was allowed to flow for 144 s (1169 to 1313 s). We have repeated the same measurement multiple times up to 126 min, as shown in [Figure S4a](#). To prove that the current generation is solely due to methanol flow over 2D-MoS₂, one control experiment with normal filter paper was performed, and it showed negligible current ([Figure 1cii](#)). The fibrous nature of the paper generates an additional capillary pressure (P_c) along with pump pressure (ΔP), which controls the magnitude of the streaming current. Upon careful inspection of [Figure S4b](#), we note that the response time of the device in which the current increases to a maximum value ($I_{f\text{max}}$) is 1.4 s. In this time interval, the liquid velocity (V_L) over the surface reached a maximum due to the resultant pressure (ΔP_r) of both P_c and ΔP . Thus, there is a proportional relation between ΔP_r and I_f across the electrode. It is likely that the response time of such a flow-based device would primarily depend upon the flow rate and the properties of the liquid such as viscosity and surface tension. After reaching the maximum current ($I_{f\text{max}}$), the current falls to 60% of the maximum value and subsequently gets stabilized until the flow was switched off ([Figure S4c](#)). This is due to the fact that the capillarity force at the wet surface comes to an equilibrium condition, and as a consequence, the current becomes stable. It is also noticed that the time taken for the current to fall to the background level is much longer than the rise time ([Figure S4d](#)). The liquid–paper interface makes a microfluidic system, in which the initial fast rise in current is due to the additional effect of capillarity force along with ΔP_r . To validate this conjecture, we have conducted an experiment where we have reduced the “flow-off” period in which the paper is left to dry from 2 min to 10 s, and as a consequence, the capillarity-driven surge current ($I_{f\text{max}}$) in each on/off cycle was restricted. [Figure S5a](#) shows that I_f goes to $I_{f\text{max}}$ in the first cycle, and in the remaining two cycles, the current does not jump to $I_{f\text{max}}$ again; instead a steady behavior was seen. In the first cycle, there is an unrestricted motion of liquid due to the capillary action in the fibrous paper, but after the first cycle, the fibrous structure is filled with liquid, and thus there is no role of capillary action in the second and third cycle ([Figure S5a](#)). In [Figure S5b](#), the capillary action was retained by shortening the liquid “flow off” time, and therefore, the substrate got dried completely in between cycles and a stable current was observed. We have also flowed methanol over MoS₂-coated glass and a plastic film,

as shown in [Figure S6](#), where we have not observed such a surge current. Capillarity-driven surge current can therefore be expressed in the form

$$\Delta P_r = \Delta P + P_c \quad (1)$$

and

$$I_f \propto \Delta P_r \quad (2)$$

Also, in a control experiment we observed that addition of a suction pump in front of the device generates a steady current with higher magnitude ([Figure S7b](#)) in comparison to a device with no pump ([Figure S7a](#)). The inset of [Figure S7b](#) schematically presents the experimental arrangement. We have also noticed that there is no current in the absence of net flow of liquid. This was checked by dipping the device in bulk methanol. In this case, rapid rise and fall of the current was observed due to immediate wetting of the surface ([Figure S8](#)). The inset of the figure shows the experimental procedure schematically.

As the liquid flow is responsible for current generation, it is important to understand whether the direction of the current is toward the flow direction (U_f) or not. This was understood by changing the flow direction, which results in the generation of current with opposite polarity. [Figure S9](#) represents the correlation of the flow direction and the polarity of the current. The inset of each figure illustrates the flow direction responsible for the current. We find a parallel relation between I_f and U_f . This indicates that the anion is flowing along the flow direction, and current flows opposite to it.

In addition to I_b , potential differences across the two contacts (V_f) were also recorded in an open-circuit potential (OCP) measurement, performed with a CH600A electrochemical workstation. A detailed OCP circuit diagram is illustrated schematically in [Figure S10a,b](#). Potential generation follows the same trend, as shown in the I_f - t trace. From the V_f - t trace, we observed a capillarity-driven voltage surge ($V_{f\text{max}}$) in the first few seconds, which gets stabilized subsequently to a lower value after a certain time interval, as shown in [Figure S10c](#). Potential generation decreases with decreasing polarity ([Figure S10d](#)). It should be noted that experiments were performed repeatedly on the same paper, over a period of months, which suggests long-term durability of our device.

Understanding Current Generation. For a theoretical understanding of the underlying mechanism of flow-induced current generation, we considered three essential thermodynamic factors of the liquids such as (a) dissociation constant (K_a), (b) dielectric constant (ϵ), and (c) viscosity (η). The magnitudes of these factors for different solvents were plotted against the magnitude of current generated by them under similar conditions. To do so, an experiment was performed where methanol, ethanol, and propanol were passed one after another under identical conditions and corresponding I_f values were measured. The data presented in [Figure S11](#) show that the values are 250, 100, and 20 nA for methanol, ethanol, and propanol, respectively. [Figure S12](#) represents the variation of the current with all the aforementioned factors. The I_f - $\text{p}K_a$ trace shows that the current falls linearly with the $\text{p}K_a$ value of the liquids. We find that the higher the dissociation of molecules, the higher the I_f . If we consider the first step of the mechanism to be dissociation of the molecule, we may suggest that polar protic molecules got dissociated by experiencing a dipolar interaction over the MoS₂ surface. This dipole–dipole

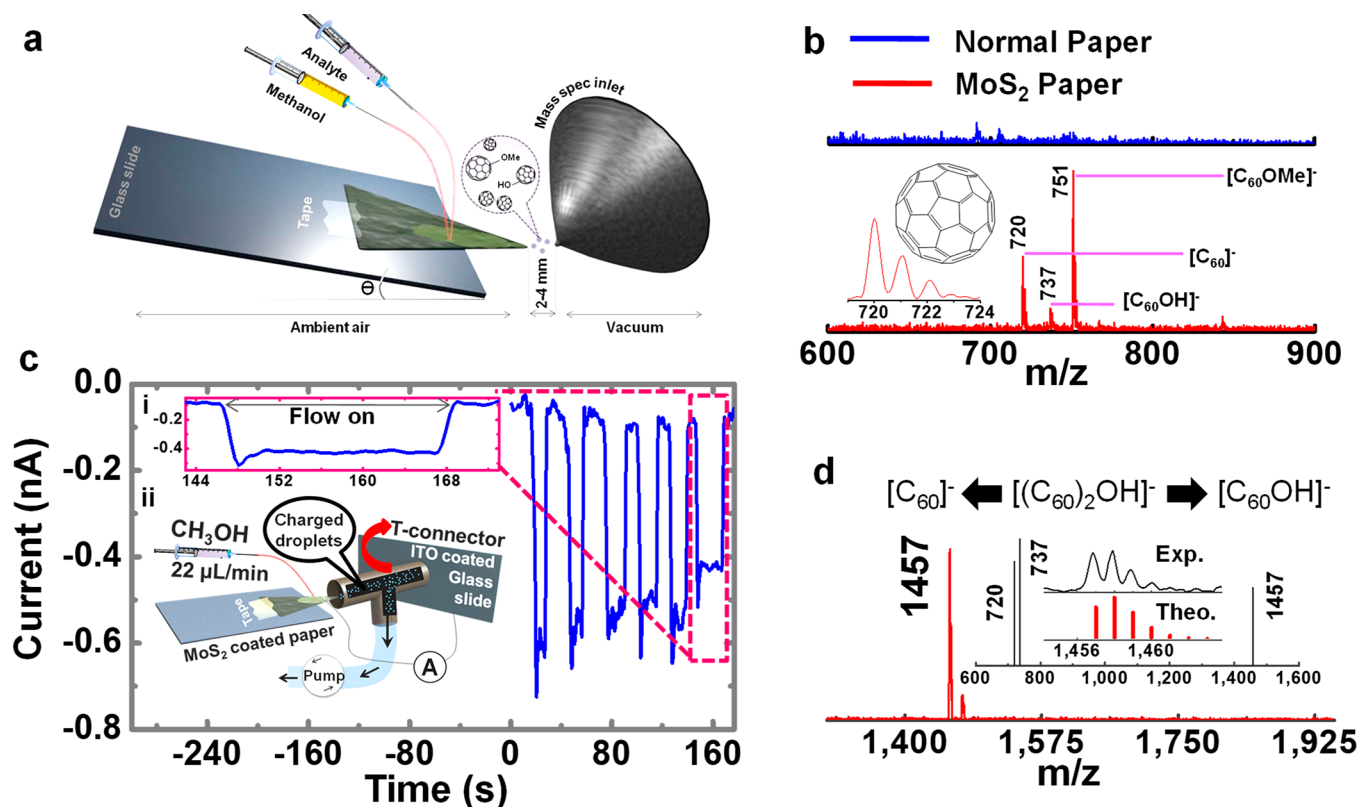


Figure 2. Streaming ionization mass spectrometry (SI-MS). (a) Schematic representation of the ion source. A MoS₂-coated triangular paper attached to a glass slide is held in front of the mass spectrometer inlet. The ion source was kept inclined with an angle of θ . The liquids are pushed through two syringes connected to separate pumps. The optimized flow rates of the solvent and the analyte pumps were 22 and 11 $\mu\text{L}/\text{min}$, respectively. The average dimensions of the triangular-shaped paper are 10 mm in width at the base and 10 mm in length. (b) Comparative SI-MS of C₆₀ using uncoated and coated MoS₂ paper. Inset shows the molecular structure of C₆₀ and the zoomed-in peak of m/z 720. (c) Current–time profile of the generated spray due to the formation of charged microdroplets. Insets: (i) Zoomed-in view of the first spray cycle and (ii) schematic view of the experimental setup. (d) Mass spectrum of the C₆₀ dimer in the selected mass range. Inset of d shows the fragmentation pattern of the peak at m/z 1457. The isotopic distribution of the peak (Exp.) at m/z 1457 is compared with the theoretical pattern (Theo.).

interaction energy (E_{dd}), in addition to the kinetic energy (E_{k}) of the molecule, drives the acid dissociation reaction. Thus, the Gibbs free energy of dissociation (ΔG^0) can be correlated with both E_{dd} and E_{k} of the molecules,

$$\Delta G^0 = E_{\text{k}} + E_{\text{dd}} \quad (3)$$

At equilibrium, ΔG^0 equals $-RT \ln K_{\text{a}}$ for the liquid. Due to less terminal velocity of the liquid (2.45 mm/s, the experimental procedure is discussed in the [Methods section](#)) over the substrate, the kinetic energy term becomes negligible in comparison to the dipole–dipole interaction energy, and hence, the above equation can be represented as $\Delta G^0 \sim E_{\text{dd}}$. Here, E_{dd} is assumed to be static and can be expressed over a distance, r , as³⁵

$$E_{\text{dd}} = l/\epsilon_0(\rho \times P_{\text{MeOH}} \times P_{\text{MoS}_2} \times \int_0^1 r_1 dr_1 / (z^2 + r_1^2)^{3/2}) \quad (4)$$

Here, ϵ_0 , ρ , P_{MeOH} , and P_{MoS_2} are the permittivity through free space, approximated number density of MoS₂ over the surface, and dipole moment of methanol and MoS₂, respectively. The parameters l and z are the distance between two silver contacts and the sum of the dipolar radii of methanol and MoS₂, respectively. Appendix 1 gives a detailed calculation of ρ . In Appendix 2, we calculated the ΔG^0 and E_{dd} quantitatively. We

found that the left-hand side and the right-hand side of [eq 3](#) are both on the order of 10^{-20} J/molecule. This validates that the dipole–dipole interaction is the driving force for the dissociation of the liquid molecules in the initial step of current generation. The other factor that governs the current generation upon the liquid flow over the MoS₂ surface is the dielectric constant of the liquid, with which we observed a linear relation with I_{f} . The $I_{\text{f}}-\epsilon$ trace ([Figure S12a](#)) shows that methanol produces higher current than propanol, linear to ϵ . On the other hand, the viscosity of the liquid shows a reciprocal relationship with I_{f} , as presented in [Figure S12b](#). In [Figure S13a](#) we have also shown that the current falls linearly with increasing $\text{p}K_{\text{a}}$ of the liquid.

Considering all the above observations, here, we propose a possible mechanism, which has been represented schematically in [Figure S14](#). It consists of two essential steps: first, dipole–dipole interaction leading to the dissociation of liquid molecules and, second, flow of anions leading to an electrokinetic current. The dissociation-induced electrokinetic effect, which resulted in a large current, can be better viewed by the Helmholtz–Smoluchowski model,³⁶

$$I_{\text{f}} = -\epsilon\epsilon_0\zeta A_c \Delta P_{\text{r}}/\eta l \quad (5)$$

and the potential gradient can be expressed as

$$V_{\text{f}} = \epsilon\epsilon_0\zeta \Delta P_{\text{r}}/\eta K \quad (6)$$

where ζ is the zeta potential of MoS₂, which is on the order of -41.2 mV (Figure S15) and A_c is the approximate area of the MoS₂ sheets. We observed a reciprocal relation between the contact distance (l) and I_p as presented in Figure S12d. There is also a linear relationship between the flow rate and the current produced (Figure S12e). The flow rate is related to the syringe pump pressure (ΔP), as shown in Appendix 4.

We have demonstrated flow-induced current using reduced graphene oxide (rGO), which produced an order of magnitude reduced current, as shown in Figure S16a. The Raman spectrum of the sample is presented in the insets of Figure S16a. Figure S16b shows the UV-vis spectrum, and the inset shows the transmission electron microscopic (TEM) image of rGO used for the experiment. The device was also tested with other liquids such as water, acetic acid, dimethylformamide, acetone, acetonitrile, dichloromethane, chloroform, toluene, and hexane (Figure S17). We observed significant current for the first three liquids.

Besides the production of current, we have found that the current is depleting in the presence of foreign molecules having very high electron affinity such as C₆₀. We have drop casted 10 μ L of C₆₀ (in toluene) during the I_f - t measurement, and we observed a sudden decrease of I_p which again gets back to its stable value after C₆₀ gets washed off (Figure S18). This provides an indication that C₆₀ may be disturbing the EDL and gets ionized at the same time, as it has high electron affinity. To prove the fact that the current depletion is not due to the effect of solvent or mechanical iteration, we performed a control experiment in which only toluene was passed along with methanol. We observed that addition of toluene does not affect the current generation, as presented in Figure S19.

Design and Characterization of the Ion Source.

Having established that flow induces a current (I_f) and the fact that addition of analyte affects I_p , we developed an ambient ion source for mass spectrometry in which in-flow molecular ionization was observed in the negative ion mode. Ambient ionization such as electrospray ionization (ESI),³⁷ paper spray ionization (PSI),^{38,39} low-temperature plasma ionization (LTP),⁴⁰ and atmospheric pressure photoionization (APPI)⁴¹ are techniques that require either a large electrical potential or a laser field to ionize molecules in solution. Although soft, they do provide some residual energy to the ion, leading to fragmentation. This limits their use in characterizing weakly bound molecular or ionic aggregates due to possible dissociation. Figure 2a schematically represents our ion source, which is a modified paper. The only difference made here compared to Figure 1 is in the shape of the paper. We changed the geometry of the paper from rectangular (in Figure 1) to an equilateral triangle to use the tip of the triangle for the generation of changed microdroplets.

Analytes of interest such as C₇₀, C₆₀, iodine, and benzoquinone were examined initially to characterize the system due to their high electron affinity in the range of 2.7 to 1.85 eV, which enables us to analyze them easily in negative ion mode.^{42–45} However, ionization of a few other analytes including amino acids, aliphatic amines, and biomolecules are also shown later in this article to demonstrate the applicability of our ion source in diverse situations. Examining the mass spectra presented in Figure 2b, it is seen that the “streaming ion source” provides soft ionization in which weak noncovalent interactions such as ion clustering through electrostatic or van der Waals interaction can also be observed. Flow of C₆₀ results in three major ion products, [C₆₀][−], [C₆₀OH][−], and

[C₆₀MeO][−], where the latter two ions are due to the clustering of C₆₀ with OH[−] and MeO[−]. These are absent in the standard mass spectrum of C₆₀ by conventional soft ionization techniques such as ESI or PSI (Figure S20). Flow of C₆₀ (as a toluene/methanol solution) on a bare filter paper shows negligible current, and therefore, we did not observe its ions (Figure 2b). To prove that the generated droplets contain high charges due to the presence of ions in it, we measured the current carried by the droplets in Figure 2c, using a setup presented in its inset.

Clustering of other species was also achieved with flow of other alcohols such as ethanol and propanol (Figure S21). All the mass assignments are based on the fragmentation pattern in the MS/MS spectra, as shown in Figures S22 and S23. We performed similar experiments with other solvents as well. Solvents such as acetone, acetonitrile, and other nonpolar solvents, which do not produce current as discussed earlier, did not cause ionization as expected (Figure S24a–e). Interestingly, DMF also shows a current and results in ionization of C₆₀. Figure S24f displays the mass spectrum of C₆₀ in DMF, where we observed a peak at m/z 764 along with m/z 720 due to the formation of [C₆₀N(CH₃)₂][−]. We have also added glucose during the ionization of C₆₀ in methanol and we observed a glucose-bound C₆₀ peak in the mass spectrum (Figure S25). This was done to see whether the $-OH$ group of glucose shows similar behavior to that shown by other alcohols. Looking at the ion chronogram of C₆₀ in Figure S26a, we can conclude that the shape of the chronogram follows a similar trend to that of the I_f - t profile (Figure 1c).

We have also performed an *in situ* measurement, in which both current due to the solvent flow over MoS₂-coated paper and the ion current of the mass spectrometer were measured simultaneously. In Figure S27a (top), we have demonstrated a flow-induced current of 0.5 μ A upon methanol flow on the MoS₂-coated paper. After a while, as the C₆₀ flow was switched on, the flow current comes to the background level; however, at the same time, ion current (Figure S27a (bottom)) in the chronogram increases to the maximum. This is due to the fact that C₆₀ gets ionized immediately when it comes in contact with the methanol stream on the MoS₂ paper. This leads to a decrease in flow current on the paper and simultaneously increases the ion current intensity in the mass spectrum. There is a time delay between decrease of flow current and corresponding increase of ion current as shown in Figure S27a (i and ii), and this is probably due to the travel time of ionized species on the electrode in solution and subsequently into the mass spectrometer. The mass spectra corresponding to C₆₀ flow, off and on, are given in Figure S27b (i and ii). Inset of the mass spectrum in Figure S27b is a schematic illustration of the experimental setup.

In addition to ion clustering of C₆₀ with different alcohols (methanol, ethanol, propanol, and glucose (methanol)), we have also observed two peaks at m/z 1457 and 1473 in the mass spectrum. Fragmentation patterns (Figure 2b) of the ions reveal that the peaks correspond to [(C₆₀)₂OH][−] and [O(C₆₀)₂OH][−], respectively. C₇₀ also ionizes similar to C₆₀ (Figure S28). The mass spectrum of benzoquinone in Figure S29a shows a molecular ion peak at m/z 108. Flowing iodine solution in methanol gives two major peaks at m/z 127 and 381, corresponding to I[−] and I₃[−], respectively (Figure S29b). Ion clustering data of a few other analytes such as tryptophan, histidine, and methylamine chloride are shown in Figure S30. Uric acid levels in body fluids are tested to diagnose gout. We

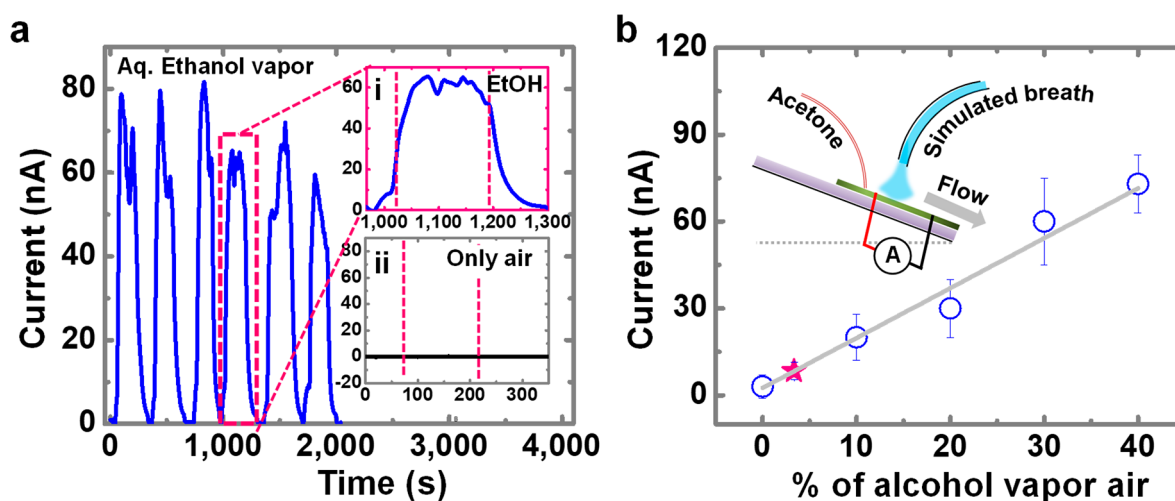


Figure 3. Flow device for the detection of alcohol in breath. (a) Current–time trace during alcohol vapor (40% aq.) exposure. Inset shows (i) zoomed-in data of one such current cycle and (ii) current generated in the absence of ethanol vapor. (b) Fitted calibration curve (gray line). The data point shown as a pink star is taken from the breath of a volunteer who had consumed alcohol. Inset of the figure schematically illustrates the device detecting simulated breath. Each experiment was repeated three times independently. Data are presented as mean, and error bar shows $\pm$ SD. The gray line is a linear fit of the generated current vs % of alcohol vapor exposed to the device. Data points were taken using standard water–ethanol solution in a glass trap and evaporating it with a nitrogen stream, and the red star corresponds to the measured alcohol concentration.

performed SI-MS of a raw urine sample (5 μ L) of a healthy individual in which we detected deprotonated uric acid at m/z 167 (Figure S31). The assignment was supported by the fragmentation data. In Figure S32, we observed mass spectra corresponding to the deprotonated peaks of propanol, benzyl alcohol, and glucose, respectively. However, by the same process we did not observe peaks in the positive ion mode (Figure S33). Generation of such deprotonated negative ions further validates our proposed mechanism, termed *dissociation-induced electrokinetic effect*. This gives strong support to the fact that the anions of the dissociated alcohol molecules move with the flow, resulting in charge separation. Movement of these negatively charged ions generates current.

We have observed that the vapors of alcohols also affect the ionization process. This phenomenon was observed in an experiment where we saw ethoxide added a C_{60} peak at m/z 765 along with the peaks at m/z 720, 737, and 751 during SI-MS of C_{60} upon exposure to ethanol vapors (Figure S34b). Here we flow C_{60} (in toluene) along with methanol prior to the exposure of ethanol vapor. The experimental setup is presented schematically in Figure S34a. The chronograms shown in Figure S34c and d prove that the interaction time of ethanol vapor is less than a few seconds. This clearly demonstrates that ethanol molecules in the vapor phase dissolve in the solution phase and undergo dissociation.

Fabrication of a Breath Alcohol Sensor. To demonstrate a potential sensing application of the device, we have used the MoS_2 -coated paper as a disposable sensor for breath alcohol detection. The device was modified in such a way that the breath of a drunken person can interact directly with the flowing liquid on the MoS_2 -coated surface. We used acetone as a flowing liquid because it does not produce current by itself (Figure S17). In Figure 3a, a simulated alcoholic breath containing 40% aqueous ethanol was blown over the device. The inset of Figure 3b shows a schematic diagram of the breath alcohol sensing device, in which simulated alcoholic breath was passed by blowing air through a liquid trap containing aqueous ethanol. A detailed description of the

device is discussed in the [Methods](#) section. We observed that the magnitude of the current varies upon the concentration of alcohol present in the vapor. For this, we changed the ethanol concentration in the vapor during the air blowing, by changing the concentration of ethanol in the liquid trap. A plot of current with concentration of ethanol is shown in Figure 3b. Table S1 shows the current measured in each repeatable experiment with different concentrations of alcohol in the mixture. Finally, the actual breath of a volunteer after 10 min of consuming 650 mL of beer containing 9% (v/v) alcohol was blown on the same paper, and the corresponding current was measured. The breath alcohol concentration was found to be less than 3% from the extrapolation of the calibration graph.

CONCLUSION

In conclusion, we have introduced a 2D- MoS_2 -coated paper-based device that generates current on the order of microamperes by flowing polar organic liquids over it. We demonstrated that the phenomenon of current generation is by a dissociation-induced electrokinetic effect in which the dissociation is driven by dipolar interactions over the MoS_2 surface. Applying the same strategy, we developed an ambient ionization source termed SI-MS, which in contrast to the conventional ion sources is power supply free, allowing soft ionization of analytes in flow. We demonstrated that SI-MS is capable of detecting loosely bound ion clusters such as $[(C_{60})_2OH]^-$, $[O(C_{60})_2OH]^-$, $[C_{60}MeO]^-$, $[C_{60}OH]^-$, I_3^- , di-, tri- and tetramers of tryptophan, dimer of histidine, and mono-, di-, and trimers of methylamine ions. The ion source is not limited by the type of liquid that is flowing. Mixed solvents such as methanol and toluene, as demonstrated for the detection of C_{60} in toluene, show the ionization of an analyte soluble in a nonpolar solvent. To demonstrate the use of the ion source in real analytical situations, we detected uric acid in raw urine during flow. It can also be utilized to characterize noncovalent interactions, such as van der Waals, electrostatic, and hydrogen bonding interactions in molecular systems of relevance to chemistry and biology. Fabrication of such an ion

source, sampling procedure, and ionization are simple, cost-effective, and eliminate safety issues during work. A potent sensing application is demonstrated for alcohol detection in the breath. The science introduced presents a method for harnessing the power of advanced materials. Our work may be utilized in the fields of sensors and microfluidics, for example, flow-based detection of specific molecules in biofluids. On the other hand, the device presented as a breath alcohol sensor can alternatively be used as a gas sensor for the detection of volatile organic compounds in ambient air.

METHODS

Synthesis of MoS₂. The 2D-MoS₂ nanostructures were synthesized from bulk MoS₂ using a chemical exfoliation method. Required chemicals for the synthesis and other experiments and a brief synthetic procedure are discussed in [Supporting Information S1a and b](#).

Fabrication of the Current Generation Device. The current generation device was built by sticking a rectangular-shaped MoS₂-coated paper on a glass slide using cellophane tape. Two silver contacts, using commercially available silver conducting paint made of polymer-coated micron-scale silver particles, were made on the paper and connected to a picoammeter (Keithley 6485). These micron-thick silver contacts were stable upon the flow of liquids and generated current for several hours. The silver paint is nonoxidizable under the conditions used due to the polymeric medium. The entire device was mounted on an xyz moving stage. A syringe pump was used to push the liquids through a silica capillary to the modified paper surface with a preferred flow rate. Fabrication of MoS₂-coated paper and design of the flow current device are presented in [Supporting Information S1d and S2a](#).

Characterization. The optical properties of as-synthesized MoS₂ were characterized by a PerkinElmer Lambda 25 UV–vis spectrometer and a CRM-Alpha300 S (WITec GmnH) Raman spectrometer. Structural features of 2D-MoS₂ were studied using high-resolution transmission electron microscopy (JEOL 3010).

The MoS₂-coated paper was characterized using Raman spectroscopy. The morphology of the bare filter paper and MoS₂-coated filter paper was observed by scanning electron microscopy (FEI Quanta 200 scanning electron microscope). Detailed characterization is briefly discussed in [Supporting Information S1c and e](#).

Fabrication of the Ion Source. The ion source is similar to the current generation device. A triangularly cut MoS₂-coated paper was fixed on a glass slide, and the tip was held facing the mass spectrometer inlet. The solutions were pushed through a capillary using a syringe pump.

Mass Spectrometric Measurements. All the mass spectrometric measurements were performed using a linear ion trap Thermo LTQ-XL mass spectrometer. Sheath gas flow rate, tube lens, and capillary voltages were set to zero. [Supporting Information S3c](#) discusses mass spectrometric details in brief.

Fabrication of the Breath Analyzer. An opened end of a silicone tube was held right above our device, while the other end of the tube was connected to a liquid trap. The aqueous ethanol solution kept inside the liquid trap was then vaporized with air flow. The generated current was measured using a picoammeter.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c09985>.

Additional information on experimental details, materials characterization, control experimental results, table for alcoholic breath analysis, and calculations on electrokinetic energy ([PDF](#))

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Author Contributions

P.B. designed and performed the electrical current generation experiments with the help of S.K.J., T.A., K.U., and S.D. The material was synthesized by B.M. and R.I. J.C. helped with the calculations leading to an understanding of current generation. P.B. wrote the initial draft of the paper with input from all the authors. The project was conceived under the supervision of T.P.

Notes

The authors declare no competing financial interest.

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