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Triboelectric effect as a new strategy for sealing and controlling the flow in paper-based devices

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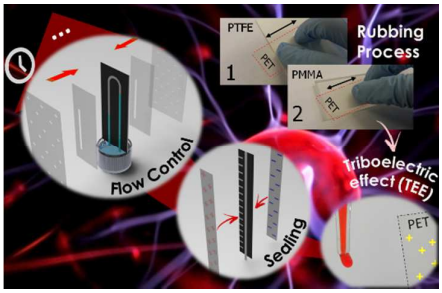

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INTRODUCTION

Microfluidic platforms made of paper are one of the simplest and cheapest alternatives to fabricate disposable and portable point-of-care devices.[1-5] The porous structure of this material provides a natural fluid delivery by capillarity, which can carry the analyte from the sample inlet to the detection zones without the need of external pumps,[6] reducing energy consumption and material wastage, besides purifying the sample by filtration or separating the analyte from complex mixtures by chromatography.[7-9] However, devices directly exposed to ambient conditions have some limitations that include risk of contamination during the transportation and/or operation and evaporation rate of the solvent, which is mainly caused by humidity changes.[10] Another important aspect of paper-based fluidic devices that is being recently studied and improved is the flow control.[11-13] In some cases the flow rate need to be increased to provide faster delivery of reagents and for other cases delayed to give more time to reactions to take place.[14] In order to contribute in these two aspects, we reported here by the first time a simple alternative to promote the sealing of microfluidic paper-based analytical devices (μPADs) and controlling its flow rate using triboelectric effect (TEE). The TEE is a theory related to contact electrification (tribocharging), which happens when two materials are brought into contact (by rubbing, for example) and then separated, creating electrostatic charges.[15] The accurate mechanism of the charge formation is still motive of debate and not completely understood[16] but these charges may be used to promote electrostatic sealing of μPADs. The charged surfaces can attract aqueous solution, delaying the fluid delivery and minimize its evaporation. The main goal of this study was to show the use of charged surfaces (by tribocharging) as a new approach to perform sealing and flow control in μPADs. The poly(ethylene terephthalate) (PET) film was charged without external voltage supply, only by rubbing its face against acrylic or Teflon surfaces.

EXPERIMENTAL

The layout of μPADs was drawn in graphical software and directly printed on Whatman #1 chromatographic paper by using a wax printer (Xerox ColorQube 8570DN). Channels were designed with 75 mm long and 2 mm wide. After printing, μPADs were submitted to a thermal treatment in a hotplate at 150°C for approximately 1 min to allow the wax penetrates into the paper pores. All the experiments were performed with the device dipped vertically into a food-dye solution (blue color) reservoir, and the fluid front (distance traveled in the channel) was monitored over time.

PET was chosen as sealing material for the microfluidic devices due to its flexibility and transparency, which allows visualization of flow assays, besides the ability that this material have to accumulate charges when rubbed (see movies in ESI†). The PET film was tribocharged by rubbing on Teflon (PTFE) or acrylic (PMMA) pieces, to obtain positively and negatively charged surfaces, respectively (Fig. 1a). Then, the paper-based device was placed between both charged PETs, as demonstrated in Figure 1b.

In a second part of this study, the possibility to control the flow of an aqueous dye solution by using the TEE was studied, as displayed in Figure 1c. For this purpose, hollow structures with different sizes were fabricated onto a PET foil by using a cutting printer (Silhouette Cameo plotter). We kept a hydrophilic portion without wax (5 mm long and 2 mm wide) as entrance for the aqueous solutions in all devices.

RESULTS AND DISCUSSION

Tribosealed μPADs and flow rate measurements

The sealing of paper-based devices is an important way to prevent contamination and evaporation of solvents in flow assays, improving the results for sensor applications and increasing the flow rate when compared to opened devices.[10] In this report, the sealing of μPADs was performed by rubbing (triboelectrification) PET foils on different materials (Fig. 1a), followed by simple electrostatic interaction between the charged PET surfaces and the paper-based device (Figure 1b). The tribosealing method is described here by the first time and its efficiency regarding the flow rate increase by

preventing the evaporation was evaluated in comparison with the opened device. Once the humidity is an important parameter in paper-based chromatography as well as for triboelectrification, the experiments were performed considering two different values (32 and 63%) at 23(±1)°C.

Figure 1d presents the distance traveled by the fluid through the paper pores over the time for both sealed and opened devices at 32% of humidity. As it can be observed, for the opened device it was necessary approximately 30 min for the liquid to flow 40 mm long in the channel, and then stops due to the evaporation, which started to prevail over the capillary force. However, for the tribosealed device, the liquid traveled through the channel 75 mm long within 10 min only, which was at least 2.5 times faster when compared with toner sealed paper-based devices.[10] This result suggests that the simple sealing method proposed here can increase the flow rate in relation to opened devices, preventing solvent evaporation as well as device contamination.

The same experiment was carried out at approximately 63% of controlled humidity and the results are presented in Fig. 1e. As it was expected, the liquid front for the opened device travelled 50 mm long through the channel in approximately 25 min before start to dry. Under this condition, the device was at least 2 times faster than with 32% of humidity, considering 40 mm of distance traveled by the fluid inside the channel, since high humidity decreases the solvent evaporation, increasing the flow rate. This result indicates that variations of humidity are critical to solvent evaporation and consequently affect the flow rate. These variations can be very serious for developing countries where humidity can change quickly influencing time-dependent reaction rates. However, no significant variations were observed for the tribosealed device, which highlights the efficiency of the proposed method and the importance of sealing step for paper-based microfluidics.

Since 1D fluid transport in porous matrices (like paper strip) during wet-out is governed by capillary force, the distance traveled by the fluid front inside the channel should range linearly with the square root of time, following the Lucas-Washburn equation:[17]

$$L = (\gamma r t \cos\theta / 2\eta)^{1/2}$$

where L is the distance travelled by the fluid front, γ is the surface tension, r is the pore radius, t is the time, θ is the contact angle between the liquid and the paper surface and η is the viscosity of the fluid. Thus, the distance L was plotted over the square root of time for both opened and tribosealed devices and the results are presented in Figures 1d and 1e (inset graphs).

The tribosealed devices presented a good linear correlation for both humidity values studied here (r^2 = 0.9941 and 0.9976 for 32% and 63% of humidity, respectively), suggesting that the mechanism of flow is essentially by capillary force. However, the same behaviour was not observed when the opened device was applied, which strongly indicates that other parameters, such as solvent evaporation, may probably interfere in the flow rate under our experimental conditions.

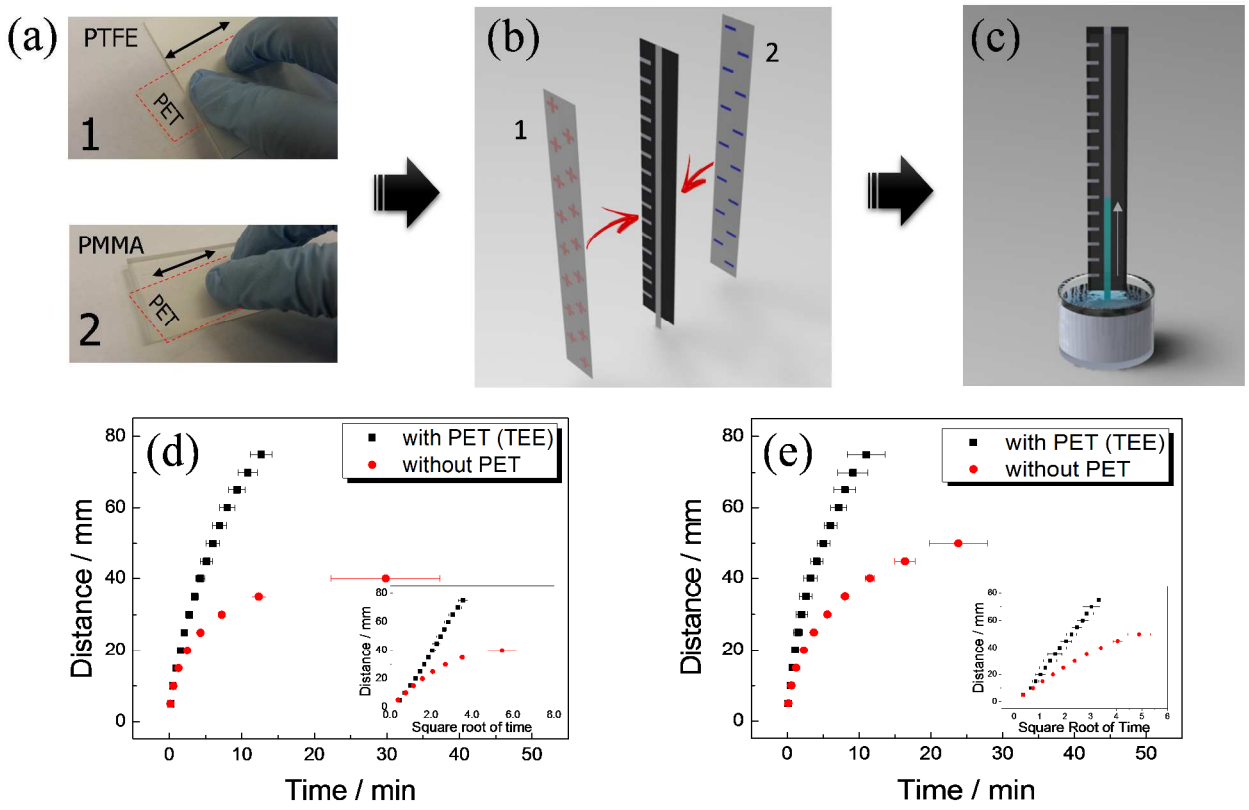

Figure 1. Images of the manual tribocharging of PET sheets by rubbing on PTFE and PMMA surfaces (a). Schematic representation of tribosealing process by electrostatic "sandwich type" contact (b) and flow measurement procedure with the µPAD vertically positioned (c). Distance traveled by the fluid front inside the paper channel over the time for the tribosealed and the opened µPADs at 32% (d) and 63% of humidity (e). In (d) and (e), the inset graphs show the distance traveled by the fluid front over the square root of time at 32% and 63% of humidity, respectively. All these experiments were performed at constant room temperature of approximately 23°C.

Influence of electrostatic charges on the flow rate

Water is one of the most common solvents used in microfluidic applications and its unique properties always attracted the attention of many researchers. Its structure has both positive and negative partial charges which may be explored to change the shape and position of water molecules.[18,19] One of the applications that involves the manipulation of water in charged surfaces is called digital microfluidics. Basically, a drop of water can be manipulated when a voltage (~50 to 100 V) is applied in an array of electrodes covered by an insulator layer.[18] The charges that were accumulated on the top of the insulator attract water molecules that were positioned adjacently to the electrode.[20] In this topic, we will describe by the first time that electrostatic charges at PET sheets can affect the capillary flow in µPADs.

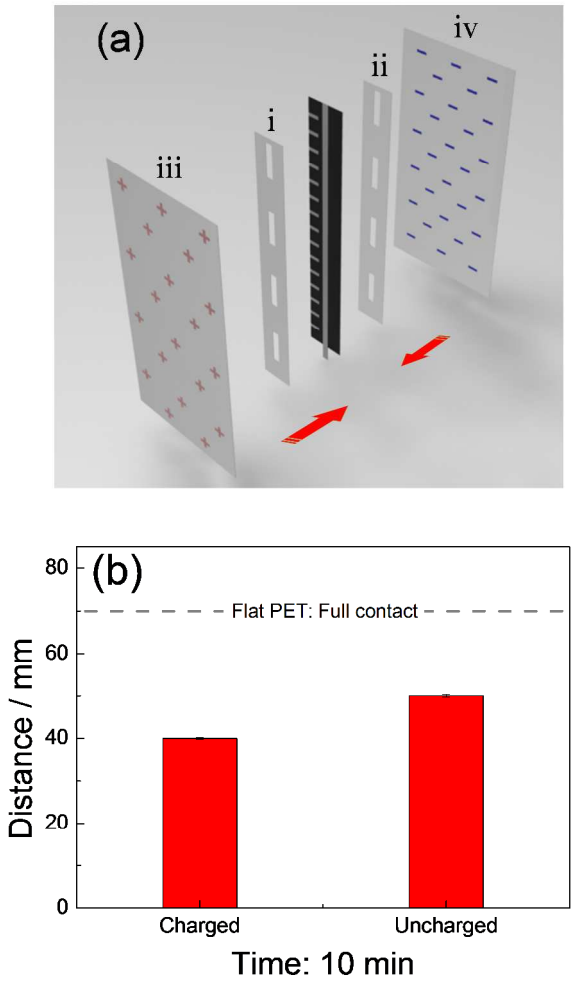

Figure 2. (a) Schematic representation of the sealing process with two hollowed PET sheets (i and ii) used as spacers and two charged PET sheets (iii and iv) used to promote the sealing and to delay the flow. (b) Distance travelled by the fluid over 10 min of measurement for the charged and uncharged devices.

First, it is important to highlight here that the accumulated charges at PET sheets can change the position of dripping water (Fig. S1 in ESI†). Next, we performed experiments to evaluate if the experimental setup described in Fig. 1b has any influence on flow of an aqueous dye solution. Our control experiments shows that distance *vs*. time curves are essentially the same when the charged PET is in direct contact with the hydrophilic channel (see Fig. S2 in ESI†). Thus, the electrostatic charges have no influence in the capillary flow rate when the PET is in direct contact with the hydrophilic channel. Our results are in agreement with the literature, where it has been reported that, due to ionic conductivity, the presence of thick layers of absorbed water could discharge the materials surface as they are separated.[21] Thus, in order to show that electrostatic charges can affect the flow in paper-based analytical devices we inserted a PET sheet with hollow structures to avoid the direct contact between the charged surface and the hydrophilic channel (Fig. 2a). The sandwich between the charged sheets (Figures 2a (iii) and (iv)) is strong enough to keep all sheets together. The distance between the charged PET surface and the hydrophilic channel is also a key factor. We kept the charged PET sheets at 100 µm (thickness of the PET sheet) from the hydrophilic channel. In order to follow the capillary flow using the sandwich layout, we measured the distance travelled by the fluid after 10 minutes of analysis. Fig 2(b) shows that charged PET sheets delays the capillary flow in about 10 mm when compared with the control experiment (same layout but without rubbing the PET sheets). This delay effect can be attributed to the presence of charges on the PET sheets surface, which attract water molecules and consequently slow down the capillary flow in the hydrophilic channel.

Flow control using TEE

Recently, the ability to control the flow in channels produced in µPADs has received considerable attention.[22,23] This control is very important in enzyme-linked immunosorbent assays (ELISAs) and DNA-based tests, because they need incubation and washing steps, for example.[22,23] For this reason, efforts have been dedicated to control the flow in paper channels, e.g. changing the geometry of the fluid path,[17,24] creating wax barriers,[25] using electromagnet and fluidic diodes,[22,26] applying pressure in a specific region of the channel,[23] and many other ways.[27] Nevertheless, the most methodologies reported in the literature take into account only the flow delay in µPADs, neglecting the importance of accelerating the flow, which can be used for more complex manipulations and to reduce the analysis time. In other hand, methods to accelerating the fluid transport in paper-based matrices are still at an early stage of development.[12,28] For this reason, we have described a new strategy for controlling the flow, which can be used in both ways, delaying or accelerating the fluid transport according to the µPAD design. Thus, the use of TEE can complement previously reported methods and provide the control of the flow in paper-based channels without any effect to the porous structure or need to change the format/shape of the hydrophilic channel. Furthermore, the PET film can be used several times, being necessary only rubbing it again to recharge the surface.

In order to illustrate how triboelectric charges can be used to control the capillary flow, "U" shaped channels with two inlet doors for the entrance of the aqueous dye solution were prepared. From now on, the hollow structures with a charged PET on the top will be called triboelectric delays (TEDs). In Fig. 3(a), it can be seen that the use of TEDs with different lengths in both sides at the same channel can tune the meeting-point spot (indicated by yellow arrows), proving that charged PET film has influence on the flow rate. The meeting-point spot was defined as the position in which the aqueous dye solution from both sides of the channel will reach each other. As it can be observed, the red rectangle presented in Figures 3a and 3b shows the size and position where TEDs were aligned to perform the flow-control experiments. Considering the concept demonstrated here, another study was carried out using TEDs in both channels (Fig. 3b). For this, a charged PET sheet without TEDs was used as

control (Fig. 3b(i)), and two TEDs with 20 and 40 mm length (Figures 3b(ii) and 3b(iii), respectively) were used for different flow delays. As it was observed, the meeting-point spot increased proportionally with the length of TEDs (Fig. 3c), which indicates that the simple proposed method can be used to delay the fluid delivery without changing the format or adding reagents to the hydrophilic channel. Fig. S3 in ESI† shows the effect of the length of TEDS in the Washburn curves.

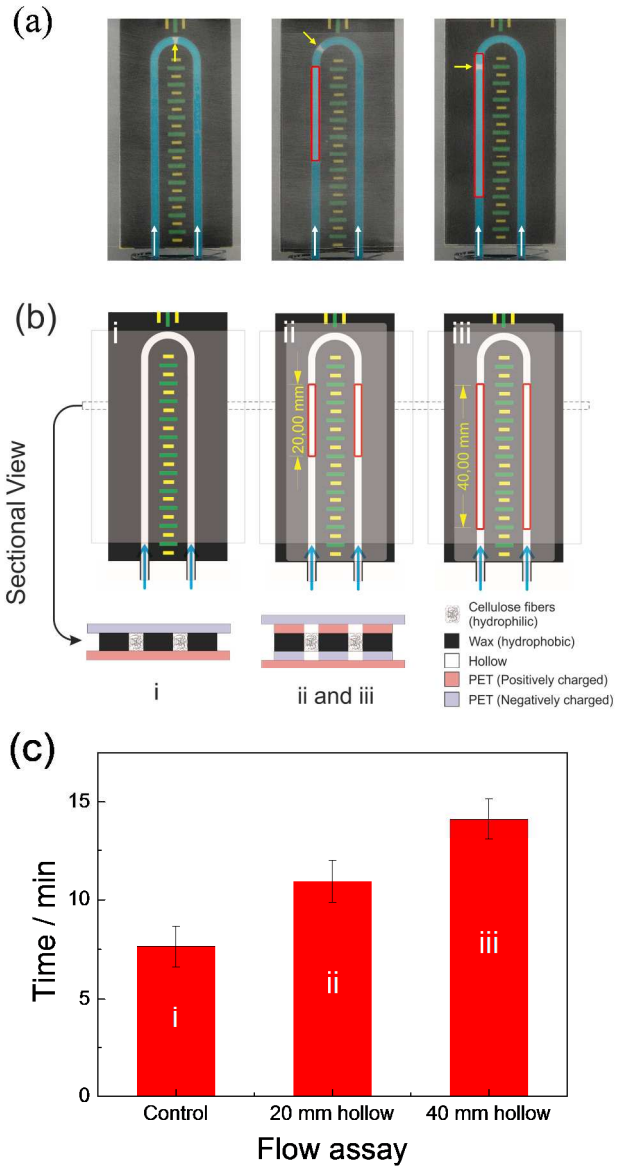

Figure 3. (a) Pictures taken during the experiment: control (i) and hollow structures of 20 mm (ii) and 40 mm (iii). The yellow arrows indicate the meeting-point of the aqueous dye solutions. (b) Experimental set up to control the flow rate by adding TEDs of different lengths in both sides of the channel. (c) Time necessary for meeting-point: control experiment (i) and hollow structures (ii and iii).

Conclusions

We reported here by the first time that triboelectric charges can be used to seal and control the flow in paper-based analytical devices. We have used a very simple and low cost process that consists in rubbing PET sheets against different materials and positioning them on paper-based devices. The triboelectric sealing is reversible, speeds up the flow rate when compared to opened devices and minimizes the effect of fluidic evaporation. Also, no equipment is necessary to generate the charges on the surface of the PET sheets. We demonstrated that triboelectric delays can be fabricated by adding hollow structures between the charged PET and hydrophilic channels. As a proof of concept, we successfully demonstrated that it is possible to delay the flow rate of an aqueous dye solution in paper-based microfluidic devices. This very simple and low cost setup can be combined with different types of paper and many other materials can be used based on the triboelectric series. This very simple method can be used to complement previously reported studies on flow control and sealing process for µPADs.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Movie 1; electroscope experiment, Movie 2; TEE on PET-paper system, Movie 3 and 4; influence of tribocharged PET on dripping water, supplementary; movie 3 and 4 explanation and control experiment. See DOI: 10.1039/c000000x/

1. W. K. Tomazelli Coltro, C.-M. Cheng, E. Carrilho and D. P. de Jesus, *Electrophoresis*, 2014, **35**, 2309.
2. A. K. Yetisen, M. S. Akram and C. R. Lowe, *Lab Chip*, 2013, **13**, 2210.
3. H. Liu and R. M. Crooks, *J. Am. Chem. Soc.*, 2011, **133**, 17564.
4. B. Li, W. Zhang, L. Chen and B. Lin, *Electrophoresis*, 2013, **34**, 2162.
5. B. J. Toley, J. A. Wang, M. Gupta, J. R. Buser, L. K. Lafleur, B. Lutz, E. Fu and P. Yager, *Lab Chip*, 2015, DOI: 10.1039/C4LC01155D.
6. S. Mendez, E. M. Fenton, G. R. Gallegos, D. N. Petsev, S. S. Sibbett, H. A. Stone, Y. Zhang and G. P. López, *Langmuir*, 2009, **26**, 1380.
7. E. T. S. G. Silva, M. Santhiago, J. T. C. Barragan and L. T. Kubota, *Anal. Methods*, 2014, **6**, 6133.
8. L. Y. Shiroma, M. Santhiago, A. L. Gobbi and L. T. Kubota, *Anal. Chim. Acta*, 2012, **725**, 44.
9. J. Noiphung, T. Songjaroen, W. Dungchai, C. S. Henry, O. Chailapakul and W. Laiwattanapaisal, *Anal. Chim. Acta*, 2013, **788**, 39.
10. K. M. Schilling, A. L. Lepore, J. A. Kurian and A. W. Martinez, *Anal. Chem.*, 2012, **84**, 1579.
11. B. J. Toley, B. McKenzie, T. Liang, J. R. Buser, P. Yager and E. Fu, *Anal. Chem.*, 2013, **85**, 11545.

12. D. L. Giokas, G. Z. Tsogas and A. G. Vlessidis, *Anal. Chem.*, 2014, **86**, 6202.
13. B. Lutz, T. Liang, E. Fu, S. Ramachandran, P. Kauffman and P. Yager, *Lab Chip*, 2013, **13**, 2840.
14. M. Santhiago, E. W. Nery, G. P. Santos and L. T. Kubota, *Bioanalysis*, 2014, **6**, 89.
15. Z. L. Wang, *ACS Nano*, 2013, 7, 9533.
16. L. S. McCarty and G. M. Whitesides, *Angew. Chem. Int. Ed.*, 2008, **47**, 2188.
17. E. Fu, B. Lutz, P. Kauffman and P. Yager, *Lab Chip*, 2010, **10**, 918.
18. A. R. Wheeler, *Science*, 2008, **322**, 539.
19. L. P. Santos, T. R. D. Ducati, L. B. S. Balestrin and F. Galembeck, *J. Phys. Chem. C*, 2011, **115**, 11226.
20. M. H. Shamsi, K. Choi, A. H. C. Ng and A. R. Wheeler, *Lab Chip*, 2014, **14**, 547.
21. L. S. McCarty and G. M. Whitesides, *Angew. Chem. Int. Ed.*, 2008, **47**, 2188.
22. X. Li, P. Zwanenburg and X. Y. Liu, *Lab Chip*, 2013, **13**, 2609.
23. J. H. Shin, J. Park, S. H. Kim and J.-K. Park, *Biomicrofluidics*, 2014, **8**, 0541211.
24. A. Apilux, Y. Ukita, M. Chikae, O. Chailapakul and Y. Takamura, *Lab Chip*, 2013, **13**, 126.
25. L. Rivas, M. Medina-Sanchez, A. de la Escosura-Muniz and A. Merkoci, *Lab Chip*, 2014, **14**, 4406.
26. H. Chen, J. Cogswell, C. Anagnostopoulos and M. Faghri, *Lab Chip*, 2012, **12**, 2909.
27. D. M. Cate, J. A. Adkins, J. Mettakoonpitak and C. S. Henry, *Anal. Chem.*, 2015, **87**, 19.
28. S. Jahanshahi-Anbuhi, P. Chavan, C. Sicard, V. Leung, S. M. Z. Hossain, R. Pelton, J. D. Brennan and C. D. M. Filipe, *Lab Chip*, 2012, **12**, 5079.