Marangoni Self-Propelled Capsules in a Maze: Pollutants 'Sense and Act' in Complex Channel Environments

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Marangoni Self-Propelled Capsules in a Maze: Pollutants ‘Sense and Act’ in Complex Channel Environments

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Environmental remediation is a highly pressing issue in the society. Here we demonstrate that autonomous self-propelled millimeter sized capsules can sense the presence of pollutants, mark sites for visible identification and remove the contamination, while navigating in a complex environment of interconnected channels, the maze. Such long-range self-powered capsules propelled by the Marangoni effect, are capable of releasing chemicals to alter the pH and induce aggregation during pollutant flocculation, at a faster rate than convection or diffusion. These devices are foreseen to have real-world environmental applications in the near future.

INTRODUCTION

Currently, self-propelled autonomous devices on the nano, micro and macro-scale are very important research areas in materials science. They have been proposed to perform biomedical tasks, such as microsurgeries and drug delivery[1,2], natural resources discovery[3] and environmental remediation[4,56]. The propulsion mechanisms of these devices, on the sub-millimeter (nano and micro) scale, use mechanisms of self-diffusionphoresis[7], self-electrophoresis[8,9] and bubble-propulsion[10] predominantly. Contrastingly, at the macro (millimeter and above) level, the dominant propulsion mechanism has been leveraging on the differences in the induced surface tension of the chemical environment, a phenomena otherwise termed as the Marangoni effect. As such, Marangoni effect propelled devices does not require external power source and can travel over large distances, surpassing several tens of meters. Therefore, such self-powered machines are extremely attractive for environmental sensing and remediation.

There have been reports on environmental clean-up of oil spills with millimeter sized Marangoni effect powered devices5 as well as microengines[11]. Recently, micromotor devices producing active oxygen species by Fenton reaction were used to spread the active decontaminant in the bulk solution to remove the polluting dye.[12] In another work, the microjet engines were used in a similar manner to stir the solution and enhance the rate of chemical reaction.[13] However, to date, there has been no report on utilizing the autonomous motion of artificial motors in complex channel environments with regards to sensing applications and pollutant removal.

Complex interconnected branching channel environment, the maze, offers capability to test the interaction of the living or inorganic systems. Typical example of utilization of maze is “maze solving” problem, finding the (shortest) route from point A to point B (start-to-finish route). It has been demonstrated that the problem of the shortest path from point A to B in the maze can be solved passing high voltage (several kV) through evacuated microfluidics network (with channel width of 250 μm).[14] Resulting glow discharge marked the shortest pathway. In similar fashion, microfluidic systems were used to find out the routes of least fluidic resistance through a maze. This method used liquid pressure driven system in microfluidics channel maze with channels of hundreds of μm in width.[15] Alternatively, the maze can be used for investigate chemotactic behaviour of organisms. The size of the maze path should be compatible with size of investigated organisms. Millimetre sized channels (~3 mm in width) were carved to test the capability of plasmodium of the slime mould (*Physarum polycephalum*) to find the shortest route towards food.[16] In similar way, 1 mm wide channels were utilized to study behavioural plasticity of worm *Caenorhabditis elegans.*These worms were also able to employ chemotaxis and find the shortest route to the source of food through the maze.[17] It was demonstrated in sub-millimeter scale that oild droplets can follow interfacial tension gradient between two liquids in simple channel to follow different paths in very simple maze-like system.[18]

Here we show how the Marangoni effect “powered” autonomous inorganic capsules can navigate in complex environments of a maze of channels; using the chemotaxis to detect the presence of chemicals; these capsule express a change in their behaviour upon detecting the chemical and are able to label the site and successfully remove pollutant molecules on the macroscale in such a labyrinthine maze.

MATERIALS AND METHODS

The experiments were carried out in a Teflon maze with most of its running pathways possessing the width of 1 cm and a depth of 1 cm. The dimension of the Teflon plate was 42 cm × 26cm × 2 cm. 200 mL of solution (water or water/modifier mixtures) was placed into the maze channel. After each individual experiment, the liquid was taken out with a pump and the maze was washed twice with 200 mL deionized water.

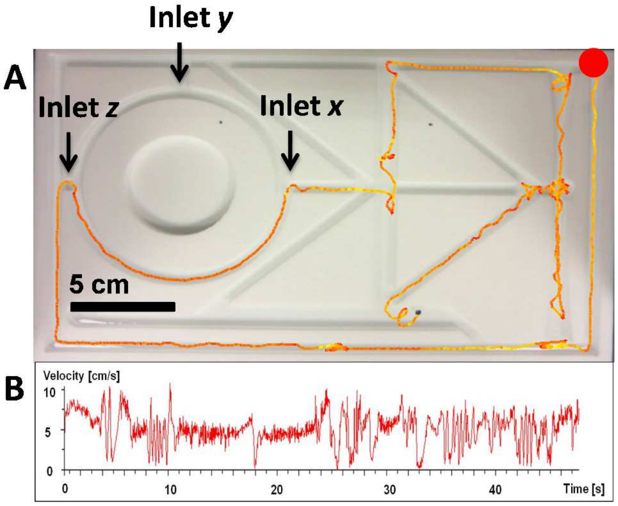

Figure 1. Motion of PSf-capsule in complex channel environment. (A) Tracking of the PSf capsule in the channel of the maze. Color code: yellow to orange, the darker shade means faster velocity. The red dot indicates the origin place of the capsule. The inlets to main circular channels are marked "x", "y" and "z" for their better identification in the text. Scale bar 5 cm. (B) Velocity profile of the running capsule. Total path length of 2.5 meters was travelled for the motor and the average velocity was 5.1 cm/s.

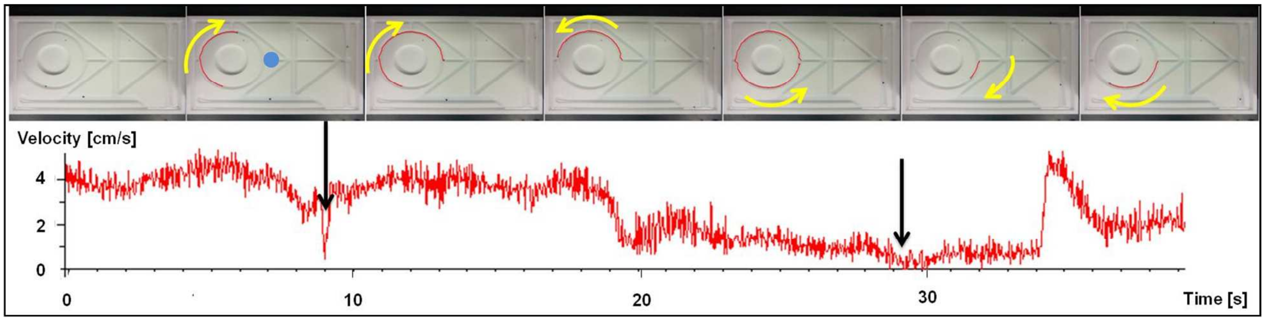

Figure 2. Interaction between the PSf capsule and the SDS containing solution. When the capsule runs near to the SDS containing solution, it is "repelled" and it reverses its direction of motion. The reversing and running of capsule shows several cycles of back and forward motion. The blue dot indicates the place of SDS solution applied. Bottom: The velocity-time profile. The arrows show the time when the capsule reached its turning point, giving an instantaneous zero velocity.

A Casio HD video-recorder was placed over the maze. The video sequences were analyzed using Nikon NIS-Elements™ software and the average velocities or angles were calculated. For each set of data, the standard deviation and average value of the recorded angles (*n*=5; five independent experiments with the same conditions) were calculated with the standard deviations shown as error bars. The capsule precursor was prepared by mixing polysulfone (PSf, Sigma-Aldrich) with *N,N'*-dimethylformamide (DMF, Merck) and was dissolved into a clear solution using an ultrasonic bath for 30 minutes. For experiments utilizing sodium dodecyl sulfate (SDS) incorporated polysulfone capsules, the amount of PSf and SDS in DMF was 7% and 4% wt., respectively. Nickel nanoparticles (1 wt %) was incorporated into the capsules to enhance the visibility. DMF was added to the mixture and sonicated for 30 minutes. Solutions were freshly prepared for each experiment. For the SDS solutions, methyl red (0.5 wt %) was mixed into the solution to enhance the visibility of the diffusion of the liquid, and the control experiment showed that there was no interaction between the methyl red containing solution and the capsules (0 mM SDS). The artificial flocculation of "pollutant" was made by mixing 40 mL of $FeCl_3$ solution (~10 mM), KI (1 M) and bleach with a ratio of 40:2:1.5 and the mixture was immediately placed into the maze channel. The imidazole incorporated capsules were made by dissolving the PSf (7 wt %) and immidazole (4.5 wt %) in DMF after 30 min of ultrasonication. Solutions of pH indicators were all 1 wt% and fresh solutions were made before use in the maze channel.

RESULTS AND DISCUSSION

We wish to demonstrate that the millimeter sized capsules are capable of sensing chemicals, signal their presence and ultimately remove them from the environment. These capsules are made from a solution of polysulfone in DMF and the loaded cargo of chemicals can be systematically released to the surroundings. When the PSf/DMF mixture (5 µL) is introduced into the aqueous solution, it immediately solidifies upon contact with water based on phase inversion.[19] Upon solidification, the pore size at the PSf/water interface is ~130 nm while pores at PSf/air interface are ~20 µm large. This leads into the slow release of DMF at the edges of capsule.5 Given the volume of the capsule (5 µL) and running time of capsule (20 min), one can establish DNF release rate to ~4 nL/second. Residual DMF is slowly asymmetrically released from the capsule, changing the surface tension of its vicinity which leads to its propulsion by the Marangoni effect. Since the surface tension (γ) of DMF/water mixture (γ_{DMF}= 35.2 mN m^{-1}) is lower than that of water (γ_{water}= 72.0 mN m^{-1}), the capsule is "pulled" towards the region of higher surface tension.

In order to study the motion of millimeter size PSf capsules in complex channel environment, we fabricated a "maze" of channels in a Teflon slab of dimensions: 42 cm × 26cm × 2 cm. The typical channels have a width of 1 or 2 cm. First, we introduced the PSf capsule into the solution-filled channel systems. The PSf capsule moved in the channel in a singular direction and when the intersections of the interconnected channels were reached, it randomly selected its path on the crossroads (Figure 1; see also Video S-1, Electronic Supplementary Information).

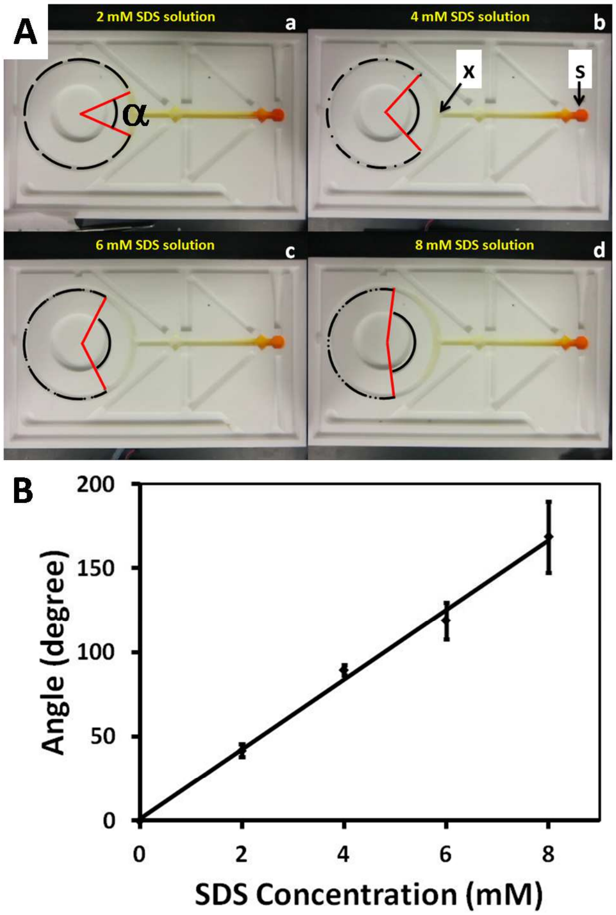

Figure 3. PSf capsule is able to sense the SDS-containing solutions and its concentration and transfer it to changes in its motion. (A) The SDS-containing solution is applied at the reservoir “s” when the capsule is reaching the point normal to the reservoir channel. As the capsule has been performing motion in circular channel, it encountered the SDS containing solution flowing into the circular channel through inlet “x” and reversed its direction. The zero-velocity point gives an angle shown in the red line. The path where the droplets moved is shown as dashed line. The reservoir channel was formed by blocking selected openings of the maze. (B) Plot showing the relationship between the angle (α) and SDS concentration (n=5).

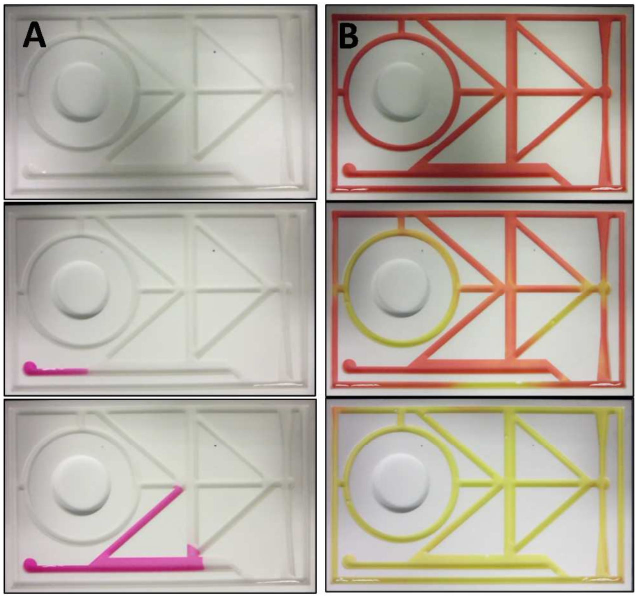

Figure 4. Act-and-sense by PSf capsule. (A) 3 g NaOH (s) placed in reservoir (A, top), it takes 5 min to to diffuse to the junction (A, bottom). The solution contains pH indicator phenolphtalein. (B) PSf capsule spreads chemical much faster. Five PSf capsules that are incorporate 4.5 wt% of imidazole can spread the chemical across all maze within 5 min. pH indicator methyl red was used to visualize this. Top: t=0, middle: t=10s; bottom: t=5 min.

To test how the PSf capsule responds to the presence of chemicals in the environment, we added SDS solution (0.1 mM, 5 μ L) to the straight channel in proximity of the inlet “x”. The other outlets (labelled “y”, “z”, see Figure 1 for their positions) were temporally tampered so that the PSf capsule could only move within the circular channel and exit over the SDS containing entrance/outlet “x”. Since the SDS/water mixture exhibits a significantly lower surface tension than water and water/DMF mixture, the capsules are repelled away from the SDS containing solution (effectively, they are actually pulled outwards from SDS containing solution by surface tension of pure water) *via* Marangoni effect. Figure 2 shows that when the capsule approached close to the SDS containing solution, it was repelled and its direction of motion was reversed. The reversing of capsule direction showed several cycles of backward and forward motion within the circular channel. The blue dot in Figure 2 indicates the location of SDS solution being applied. In the velocity-time profile, the arrows show the time when the capsule reached its turning point, giving an instantaneous zero velocity at turning point. A similar experiment was conducted to investigate whether the PSf capsule can sense the presence of surfactant and its concentration and it is demonstrated in Figure 3. The solution of surfactant (SDS) at different concentrations was introduced at a distance of ~20 cm from the entrance of circular channel (Figure 3,A, black arrow with label “s” shows at the point where the SDS solution was introduced). The outlets “y” and “z” were closed and only outlet “x” was left open. For better visibility, the SDS solution was pre-mixed with methyl red (0.5 wt %). The SDS solution spreads by convection and diffusion, reaching the entrance of the circular channel. Since the solution containing SDS exhibits lower surface tension[20] than water, the polysulfone capsule, which movement is based on difference in surface tension of water and DMF, is pulled towards place where the surface tension is the highest (water).5 Therefore when it reaches SDS containing solution, it will appear that PSf capsule is repulsed by it. If no boundaries are applied to the system, the strength of the repulsion is difficult to quantify as the direction of the motion is largely random. However, if the motion of PSf capsule is restricted by the walls of the channel, one can quantify the concentration of SDS. In order to follow measurable quantity, we used circular channel for motion of PSf capsule with one inlet where SDS can flow in and influence the motion symmetrically. The motion of the PSf capsule in circular channel is then restricted in the above noted “back-and-forth” style. With increasing concentration of from 2 to 8 mM SDS (see Figure 3, A, a-d), the difference in surface tension of water and solution containing SDS increases and this difference leads into the larger apparent repulsion of PSf capsule from the inlet of the circular channel. This is depicted in Figure 3, A showing the portion of the channel to which PSf is limited as dashed line. We postulate

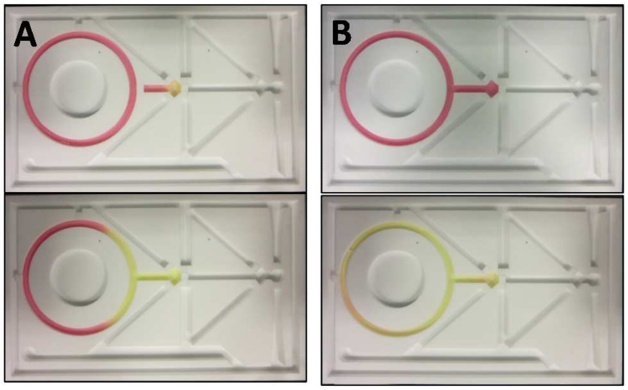

Figure 5. Enhanced diffusion of basic compound into the maze channel. (A) Only diffusion takes place: 100 µL 4.5 wt% imidazole was placed in the reservoir, and the base solution was never able to diffuse to the whole channel. (B) Self-propelled PSf-capsule induced enhanced diffusion: with the application of one capsule that is incorporated with 4.5 wt% of imidazole, it took 1 min for the whole channel of the maze to change color. The pH indicator methyl red was premixed in the water.

the angle (α) between two turning points of PSf capsule as measure to quantify the repulsion strength and hence the concentration of SDS (Figure 3,A). It can be clearly observed that α increases as concentration of SDS increases in a linear fashion (Figure 3, B). This demonstrates that the capsules are not only able to sense presence/absence of surfactant, but also the concentration.

The PSf capsule is not only able to sense chemicals in its environment, but also effectively spread them, while performing its role as a chemical sensor. Figure 4 shows the channels filled with water containing pH indicators. When we introduced solid NaOH pellet to the “maze” system, the pH of solution started to slowly change as the NaOH was being dispersed by convection and diffusion (Figure 4, A), extending into two arms of channel after 5 min, as indicated by color change in phenolphthalein. This pH change took place at 16.7% (RSD 3.7%; *n*=4) of the channel volume in 5 min, based on indicator color change. When five PSf capsules loaded with imidazole were introduced at a distance of ~20 cm from the entrance of the circular channel, the liquid in the whole maze changed pH within 5 minutes (Figure 4, B; pH indicator, methyl red). The pH was changed at 92.8% (RSD 3.4%; *n*=4) of the total channel volume of the channels when using PSf to disperse the imidasole (indicated by color change). In a similar system, if we allowed the imidazole to enter the circular channel only by diffusion (Figure 5, A), the solution in circular channel didn’t change pH even after 1 h due to the slow diffusion/convection of the imidazole molecules (note that diffusion in liquids is in general a slow process). More specifically, the pH changed only at 47.3% (RSD 14.3%; *n*=4) of the total channels volume (as indicated by color change of the indicator) after one hour. However, when the PSf capsule loaded with imidazole was introduced to the entrance of the channel and allowed to run, the pH of liquid in the circular channel was changed within 1 min (Figure 5, B) due to the fact that PSf capsule releases imidasole on its move. The change of pH was in this case almost complete, 94.35% (RSD 1.9%, *n*=4) of the total channel volume underwent pH change after 1 min when the PSf capsules were used, as indicated by color change.

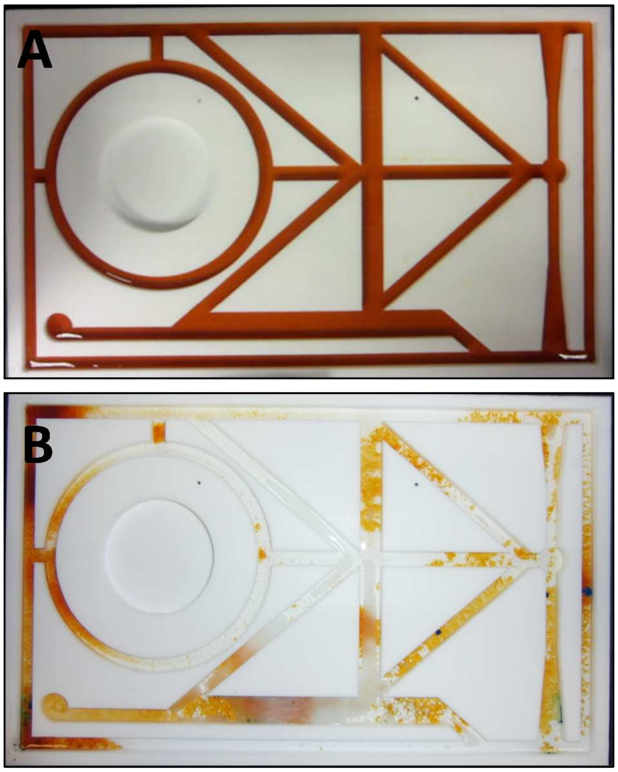

Figure 6. Environmental clean-up using SDS-incorporated capsule motors. (A) The maze channel was filled up with pollutant. (B) After application of the capsules, the flocculated pollutant can be gathered for easier removal.

Variation on the same experiment with a different channel set-up is shown in Figure S-1, Supporting Information, to show that this is the generally observed with the imidazaole-loaded capsules.

Environmental remediation is an important issue. It has been previously demonstrated that bubble-powered micromachines can remove oil droplets by attaching them to their surface4 or that they can catalyze on their surface the chemical transformation.[11,12] However, it has not been yet demonstrated that self-propelled autonomous micro or millimetre sized device spreads chemical which decontaminate the solution. Here we show such example where the PSf capsule can be loaded with chemicals, which serve to aggregate the pollutant flocculation. Firstly, we have placed Fe^{3+} and flocculants into the channels (Figure 6). The uniformly brown solution of flocculated Fe^{3+} is homogenously dispersed in polluted solution. When we introduce PSf capsule itself, the solution does not change its state. However, when we load the PSf capsule with chemical which strongly changes the surface tension in the vicinity of the capsule, the situation changes. When we introduce PSf capsule loaded with SDS, this is capable to induce the aggregation of the pollutant flocculation. The PSf capsule loaded with SDS moves over the polluted solution and “sweeps” the flocculated pollutant. We employed three PSf-SDS capsules (Figure 6) and within 2 minutes, the flocculation aggregates were swept by capsules and accumulated by the capsule and most part of the aqueous solution was cleared from pollutant which had been flocculated. More specifically, the average pollutant coverage after the application of capsule is 37.2% (RSD 10.2, *n*=5). The enhanced aggregation and gathering of the flocculation resulted in an easier removal of the pollutant from the solution. Figure S-2 (SI) shows the same case of flocculation of the pollutant by SDS loaded PSf capsule in a different channel set-up. Such “smart” removal of the coagulated pollutants coffers interesting alternative to current passive way of coagulated pollutants removal by filtration, which is the standard method in this field.[21]

CONCLUSION

We have demonstrated that PSf capsules are capable to move in a complex channel structure with multiple intersections using the Marangoni effect as driving force. Such PSf capsules can sense chemicals from large distances, extending several tens of centimeters and adapt their motion accordingly. The pattern of motion changes accordingly with chemical concentrations in the surroundings, illustrating the chemotactic biomimetic behaviour of such capsules. The PSf capsule is able to release the chemical molecules it contains, remediating the environment within a complex structure of channels, such as buffering pH changes. Capsules are also able to quickly and actively aggregate flocculent molecules in order to remove pollutants from the environment. Such chemotactic behaviour of macroscopic capsules shall lead into practical applications for environmental remediation as they do not require external source of energy or fuel for their motion, and they are able to act in macroscale (real-world size) environments and in a complex channel structure.

Acknowledgements

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Electronic Supplementary Information available from the authors or at www.rsc.org. It contaims schematic drawing of the maze, Figures S1-S3 and Video S-1.

Notes and references

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1 A. A. Solovev, S. Sanchez, M. Pumera, Y. Mei, O. G. Schmidt, *Adv. Func. Mater.*, 2010, **20,** 2430.
2 A. A. Solovev, X. Wang, D. H. Cracias, S. M. Harazim, C. Deneke, S. Sanchez, O. G. Schmidt, *ACS Nano*, 2012, **6,** 175 1.
3 A. Sen, M. Ibele, Y. Honga, D. Velegol, *Faraday Discuss*. 2009, **143,** 15.
4 M. Guix, J. Orozco, M. García, W. Gao, S. Sattayasamitsathit, A. Merkoçi, A. Escarpa, J. Wang, *ACS Nano* 2012, **6,** 4445.
5 G. Zhao, T. H. Seah, M. Pumera, *Chem. Eur. J.* 2011, **17,** 12020.
6 T. H. Seah, G. Zhao, M. Pumera, *Chem. Plus. Chem.* 2013, **78**, 395
7 A. Sen, M. Ibele, Y. Hong, D. Velegol, *Farad. Discuss*., 2009, **143,** 15.
8 S. Sanchez, M. Pumera, *Chem.–Asian J.,* 2009, **4,** 1402.
9 M. Pumera, *Nanoscale,* 2010, **2,** 1643.
10 Y. Mei, A. A. Solovev, S. Sanchez, O. G. Schmidt, *Chem. Soc. Rev.,* 2011, **40,** 2109.
11 M. Guix, J. Orozco, M. Garcıa, W. Gao, S. Sattayasamitsathit, A. Merkoci, A. Escarpa, J. Wang, *ACS Nano*, 2012, **6,** 4445.
12 L. Soler, V. Magdanz, V. M. Fomin, S. Sanchez, O. G. Schmidt, *ACS Nano*, 2013, **7,** 9611.
13 J. Orozco, G. Cheng, D. Vilela, S. Sattayasamitsathit, R. Vazquez-Duhalt, G. Valdes-Ramirez, O. S. Pak, A. Escarpa, C. Kan, J. Wang, *Angew. Chem. Int. Ed.* 2013, DOI:10.1002/anie.20130807
14 D. R. Reyes, M. M. Ghanem, G. M. Whitesides, A. Manz. *Lab Chip*, 2002, **2**, 113.
15 M. J. Fuerstman, P. Deschatelets, R. Kane, A. Schwartz, P. J. A. Kenis, J. M. Deutch, G. M. Whitesides, *Langmuir* 2003, **19**, 4714
16 T Nakagaki, H. Yamada, Á. Tóth, *Nature* 2000, **407**, 470.
17 J. Qin, A. R. Wheeler, *Lab. Chip.* 2007, **7**, 186.
18 G. K. Kurup, A. S. Basu, Proceedings of the Conference on Miniaturized Systems for Chemistry and Life Sciences 2011, MicroTAS 2011, vol. 2, Pages 1367-1369.
19 S. Sanchez, M. Roldan, S. Perez, E. Fabregas, *Anal. Chem.* 2008, **80,** 6508.
20 O. Ozdemir, S. I. Karakashev, A. V. Nguyen, J. D. Miller, *Miner. Eng.* 2009, **22**, 263
21 a) Hermann H. Hahn, H. George Hahn, E. Hoffman, H. Odegaard Chemical Water and Wastewater Treatment , WA Publishing, 2004, b) Water Treatment by Enhanced Coaguation; Operational Status and Optimization Issues; Techneau D 5.3.1a Manual 2006.