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# Automatic molecular collection and detection by using fuel-powered microengines<sup>†</sup>

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We design and fabricate a simple self-powered system to collect analyte molecules in fluids for surface-enhanced Raman scattering (SERS) detection. The system is based on catalytic Au/SiO/Ti/Aglayered microengines by employing rolled-up nanotechnology. Pronounced SERS signals are observed on microengines with more carrier molecules compared with the same structure without automatic motions.

The manipulation and detection of molecules on a micro-chip is of great interest in bioanalysis, optofluidics and lab-on-achip research, aiming at simplification, reduction of costs, and ease of reproducibility.<sup>1-4</sup> Particular attention has been given to on-chip surface-enhanced Raman scattering (SERS), which is capable of 'fingerprinting' materials from very small volumes, making it suitable for analysis on the microchip size scale.<sup>4-8</sup> When considering SERS, it is crucial that the analyte molecules must be in close proximity to the metal nanostructures within the detection volume and that the attached molecule number is theoretically proportional to the SERS intensity.9,10 Thus various methods have been adopted to capture and collect analyte molecules, such as optical,<sup>11</sup> electrokinetic,<sup>12</sup> mechanical,<sup>13</sup> magnetic<sup>14</sup> and acoustic methods.<sup>15</sup> Moreover, chemical methods are also applied for molecule attachment, recognition and specific detection.<sup>16-18</sup> Such manipulation techniques are capable of high levels of control, consistency, and repeatability. However, the high cost and the complexity of additional manipulation components are motivating and stimulating new routes and principles for practical integrated microchips.

Recently, self-propelled and fuel-powered catalytic microengines have been reported<sup>19–28</sup> and their transporting function has been developed for applications such as drug delivery,<sup>29</sup> environmental remediation<sup>30</sup> and target protein capture.<sup>31</sup> Inspired by this, we find that a microengine can be an excellent candidate to act as a cheap and reliable on-chip system for molecule collection and detection. Here we demonstrate that fuel-powered and Au-coated microengines can work as molecule collectors in the hydrogen peroxide  $(H_2O_2)$  fuel. The microengines move autonomously by an oxygen-bubble propulsion mechanism, adsorbing analyte molecules on the passage to facilitate the following SERS measurement without inducing any stimuli. In addition, we study the plasmonic geometries of microengines and tailor the concentration of H<sub>2</sub>O<sub>2</sub> to tune the collection and detection effect. The design of automatic molecular collection and detection provides another idea for boosting SERS, which simplifies molecule manipulation, potentially helping to create lower-cost devices with other detection schemes.

Fig. 1 displays the schematic of the molecule collection and detection system based catalytic tubular microengines. We fabricated tubular microengines based on Au/SiO/Ti/Ag-layered microtubes by employing polymer-based rolled-up nano-technology.<sup>32,33</sup> Pre-stressed Au/SiO/Ti/Ag-layered nano-membranes on a polymer sacrificial layer are released from the



**Fig. 1** Schematic illustrations: (I) the fabrication process of Au/SiO/Ti/ Ag tubular microengines by employing rolled-up nanotechnology and (II) the microengines adsorbed analyte molecules (R6G) in the fluids for SERS measurement.

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substrate surface by removing the sacrificial layer with a solvent, and they roll-up into a microtube to form a tubular structure.33 This material combination is selected based on the feasibility of the roll-up process and the desire for different functions. Gold is a reasonably inert metal and it claims an excellent application in the field of SERS. Besides, gold shows great potential as it is historically the most studied material for self-assembled monolayers and compatible with cells for further modifications.<sup>34</sup> Titanium provides structural support for microengines and silicon monoxide serves as a space layer. Last but not least, silver acts as a catalyst, which is well confined inside the tube to decompose H<sub>2</sub>O<sub>2</sub> into water and oxygen. Rhodamine 6G (R6G) is chosen as the analyte molecule in this study because of its reliable SERS signal and it acts as a universal organic dye in bioanalysis. Above all, as a nitrogen-containing cationic dye, R6G can be adsorbed on the gold surface by an electrostatic force and N-Au interaction.<sup>10,35</sup> In this way, we manage to collect R6G molecules to tiny volumes with the microengine as a carrier.

To benefit the detection process, it is necessary to focus on the SERS property of the microengine itself. Our former work has verified the SERS potential of a tubular structure.<sup>36</sup> As for the current system, we tuned the SERS by changing the gold layer thickness. The diameter of the microtube varies from 8  $\mu$ m to 16  $\mu$ m as the gold layer thickness increases from 5 to 13 nm (Fig. 2a). The one with a 5 nm gold layer thickness has an outstanding SERS performance (Fig. 2b), thus it is selected as the microengine. We ascribe this to the tiny plasmonic structures at the surface of the microengine, which is illustrated by a typical atomic force microscopy (AFM) image



Fig. 2 (a) The diameter of the microtube as a function of gold layer thickness. The scale bar in the optical image is 10  $\mu$ m. (b) Comparison of SERS spectra of the 10<sup>-6</sup> M R6G molecules dropping on microtubes with different gold layer thicknesses. (c) AFM morphology (1.0  $\times$  1.0  $\mu$ m<sup>2</sup>) of a microengine at the surface. The inset shows the simulated EM field distribution map of the rough surface.

(Fig. 2c). To study the SERS, a finite-difference time-domain (FDTD) method was employed to illustrate the excitation of the localized surface plasmon (LSP) modes by calculating the electromagnetic (EM) field on the microengine surface, as shown in the inset of Fig. 2c. The simplest geometry is chosen for simulations and the strongest fields are concentrated in the gaps of the rough surface. Our calculation shows that these LSP modes are able to produce maximum local enhancement as large as  $10^5$  in the Raman signal of the molecules adsorbed at these V-shaped gaps (see the ESI† for more details).

Fig. 3a shows a scanning electron microscopy (SEM) image of a typical single Au/SiO/Ti/Ag tubular microengine with a



Fig. 3 (a) SEM image of a typical single microengine with a diameter of ~8 µm. (b) Optical image of the Au/SiO/Ti/Ag microengine trajectory (yellow line) in the presence of a concentration of 3.64% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G. (c) Optical image of a dried microengine after the collecting process in a concentration of 3.64% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G. (d) The corresponding Raman intensity map of the characteristic R6G Raman peak at 1650 cm<sup>-1</sup> derived from (c). (e) Comparison of SERS spectra of the 10<sup>-6</sup> M R6G molecules in different cases. R6G molecules collected on (i) active microengines in the system (3.64% H<sub>2</sub>O<sub>2</sub>); (ii) inactive microengines (without H<sub>2</sub>O<sub>2</sub>); (iii) microengines fixed on the substrate (3.64% H<sub>2</sub>O<sub>2</sub>); (iv) a clean silicon wafer without microengines (3.64% H<sub>2</sub>O<sub>2</sub>). The inset figure shows the quantitative enhancement comparison at 1650 cm<sup>-1</sup>.

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diameter of around 8 µm. The movement of the microengine involves a bubble recoiling mechanism as that of Pt-based microengines, which relies on the catalytic decomposition of  $H_2O_2$  into gaseous  $O_2$  and water at the inner surface of the tube wall.<sup>33,37</sup> By immersing the tubular microengine into the  $H_2O_2$  solution, microbubbles are generated inside the tube and are ejected with a certain frequency from the tube openings, propelling itself to move. The trajectories of tubular Au/SiO/Ti/Ag microengines in the presence of a concentration of 3.64% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G is shown in Fig. 3b, taken from Video S1 in the ESI.<sup>†</sup> The drying process is necessary to facilitate the SERS detection. Fig. 3c displays a dried microengine after a collecting process in a concentration of 3.64% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G, and the corresponding Raman intensity map of the characteristic R6G Raman peak at 1650 cm<sup>-1</sup> is shown in Fig. 3d, which shows excellent collection and detection uniformity (see the ESI<sup>†</sup> for more details).

Nevertheless, did we actually increase the analysis molecules attached to the microengines for boosting SERS? Fig. 3e displays the typical Raman spectra of R6G molecules collected in different cases. Many peaks emerge as for the active microengines (case i, 3.64% H<sub>2</sub>O<sub>2</sub>), prominently at 612, 773, 1362, 1507, 1574, and 1650  $\text{cm}^{-1}$ , which can be assigned to the totally symmetric modes of the in-plane C-C stretching vibration.<sup>38</sup> The contrast of quantitative enhancement (at  $1650 \text{ cm}^{-1}$ ) is illustrated in the inset figure, which also shows the standard error obtained by analyzing the spectra measured at 10 different locations on different microengines (see Table S1 in the ESI<sup>†</sup> for details). Due to the difference in the adsorbed molecule number, the larger error of case i is expected. The average Raman signal from the sample treated in the molecule collection system (black, case i) is about five times as intense as that obtained from the inactive microengines (red, case ii), which represents a traditional collection method for SERS by simply dropping and drying without H<sub>2</sub>O<sub>2</sub>. The green spectrum shows the case that R6G molecules collected by dropping on microengines fixed on the substrate (case iii, 3.64% H<sub>2</sub>O<sub>2</sub>), which has much lower SERS enhancement than case i. The blue spectrum serves as a blank reference by measuring dried R6G  $(10^{-6} \text{ M})$  on a clean silicon wafer (case iv, 3.64% H<sub>2</sub>O<sub>2</sub>, without microengines), which shows no signal. These results clearly indicate that active microengines serve as effective carriers of analyte molecules, making a contribution to extending the molecule adsorption path and increasing the capture probability. The SERS enhancement factor of R6G on active microengines achieves a maximum of  $5 \times 10^5$  (see the ESI<sup>†</sup>), which can be attributed to the "hot spots" effect on the gold surface and the molecular collection effect via catalytic motions. In the current work the "hot spots" effect of the gold surface is not fully optimized and can be improved for further study.

Furthermore, Raman measurements were performed on the microengines in different concentrations of  $H_2O_2$  fuel containing  $10^{-6}$  M R6G to tune the molecule collection efficiency. The speed of the bubble-driven Au/SiO/Ti/Ag microengines is

strongly dependent on the concentration of H<sub>2</sub>O<sub>2</sub>, which influences the radius and frequency of the generated oxygen bubbles.<sup>23</sup> The microengine trajectories in 7.5 s in the presence of different concentrations of H<sub>2</sub>O<sub>2</sub> fuel (0.73%, 3.64%, 7.28%) containing  $10^{-6}$  M R6G are shown in Fig. 4a–c, taken from Videos S2-S4 in the ESI.† As we expected, the microengine in a higher concentration of H<sub>2</sub>O<sub>2</sub> fuel has a longer movement distance in the same time. The corresponding speeds of catalytic microengines in different concentrations of H<sub>2</sub>O<sub>2</sub> fuel (0.73%, 3.64%, 7.28%) are shown in Fig. 4d. Fig. 4e shows the SERS spectra comparison of 10<sup>-6</sup> M R6G adsorbed on the microengines collected in different concentrations of H<sub>2</sub>O<sub>2</sub> fuel. The inset figure shows the quantitative enhancement comparison at 1650 cm<sup>-1</sup> (see Table S2 in the ESI<sup>†</sup> for details). The system with a 3.64% concentration of  $H_2O_2$  has an outstanding SERS characteristic, owing to a higher molecule collection efficiency than a lower fuel concentration. The



**Fig. 4** Optical images of Au/SiO/Ti/Ag microengine trajectories in 7.5 s in the presence of a concentration of (a) 0.73%  $H_2O_2$  fuel; (b) 3.64%  $H_2O_2$  fuel; (c) 7.28%  $H_2O_2$  fuel. The scale bar is 100 µm. (d) Speed of catalytic microengines in (a)–(c). (e) SERS spectra comparison of  $10^{-6}$  M R6G adsorbed on the microengines collected in different concentrations of  $H_2O_2$  fuel (0.73%, 3.64%, 7.28%). The inset figure shows the quantitative enhancement comparison at 1650 cm<sup>-1</sup>.

SERS intensity of the microengines in a 7.28% concentration of  $H_2O_2$  turns out to be extremely weak, probably because larger speed is not suitable for molecule attachment. It also should be noted that the oxidation bleaching of a high concentration of  $H_2O_2$  (7.28%) can weaken the activity of R6G molecules, resulting in a lower SERS performance. Besides  $H_2O_2$ , there are other components that can be used as the fuel for microengines, suitable for extremely acidic environments<sup>39</sup> or seawater.<sup>40</sup> A suitable fuel without negative influence for automatic collection of microengines might enable clean and efficient molecule detection in further studies.

### Conclusions

In conclusion, we have designed a simple system for molecule collection and detection based on catalytic Au/SiO/Ti/Ag microengines by employing rolled-up nanotechnology and the Raman spectrum. These self-propelled microengines fueled by  $H_2O_2$  adsorb analyte molecules in fluids, acting as molecule carriers. Furthermore, optimized collection efficiency of the system is achieved by controlling the fuel concentration. Finally, a pronounced SERS signal from R6G attached to the microengine is observed, which indicates outstanding molecule collection performance. Such a molecule collection and detection system could extend the scope of applications for bioanalysis and labon-a-chip towards new designing routes.

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#### Notes and references

- 1 J. Godin, C. H. Chen, S. H. Cho, W. Qiao, F. Tsai and Y. H. Lo, *J. Biophotonics*, 2008, **1**, 355.
- 2 A. A. Kayani, K. Khoshmanesh, S. A. Ward, A. Mitchell and K. Kalantar-zadeh, *Biomicrofluidics*, 2012, **6**, 031501.
- 3 J. Wang, *Nanomachines: Fundamentals and Applications*, Wiley-VCH, Weinheim, Germany, 2013, ISBN 978-3-527-33120-8.
- 4 A. F. Chrimes, K. Khoshmanesh, P. R. Stoddart, A. Mitchell and K. Kalantar-zadeh, *Chem. Soc. Rev.*, 2013, **42**, 5880.

- 5 L. X. Chen and J. Choo, *Electrophoresis*, 2008, 29, 1815.
- 6 M. Hu, F. S. Ou, W. Wu, I. Naumov, X. M. Li, A. M. Bratkovsky, R. S. Williams and Z. Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 12820.
- 7 E. C. Lin, J. Fang, S. C. Park, F. W. Johnson and H. O. Jacobs, *Nat. Commun.*, 2013, 4, 1636.
- 8 C. Wang and C. X. Yu, *Nanotechnology*, 2015, 26, 092001.
- 9 I. M. White, S. H. Yazdi and W. W. Yu, *Microfluid. Nano-fluid.*, 2012, **13**, 205.
- 10 Y. Q. Wang, B. Yan and L. X. Chen, *Chem. Rev.*, 2013, **113**, 1391.
- 11 H. Hwang, D. Han, Y. J. Oh, Y. K. Cho, K. H. Jeong and J. K. Park, *Lab Chip*, 2011, **11**, 2518.
- 12 A. F. Chrimes, A. A. Kayani, K. Khoshmanesh, P. R. Stoddart, P. Mulvaney, A. Mitchell and K. Kalantarzadeh, *Lab Chip*, 2011, **11**, 921.
- 13 C. D. Syme, N. M. S. Sirimuthu, S. L. Faley and J. M. Cooper, *Chem. Commun.*, 2010, 46, 7921.
- 14 J. R. Basore and L. A. Baker, Anal. Bioanal. Chem., 2012, 403, 2077.
- 15 J. S. Jeong, J. W. Lee, C. Y. Lee, S. Y. Teh, A. Lee and K. K. Shung, *Biomed. Microdevices*, 2011, 13, 779.
- 16 J. Orozco, A. Cortés, G. Z. Cheng, S. Sattayasamitsathit, W. Gao, X. M. Feng, Y. F. Shen and J. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 5336.
- 17 M. Masetti, H. Xie, Z. Krpetić, M. Recanatini, R. A. Alvarez-Puebla and L. Guerrini, *J. Am. Chem. Soc.*, 2015, 137, 469.
- 18 R. W. Taylor, T. C. Lee, O. A. Scherman, R. Esteban, J. Aizpurua, F. M. Huang, J. J. Baumberg and S. Mahajan, *ACS Nano*, 2011, 5, 3878.
- 19 T. E. Mallouk and A. Sen, Sci. Am., 2009, 300, 72.
- 20 K. M. Manesh, M. Cardona, R. Yuan, M. Clark, D. Kagan, S. Balasubramanian and J. Wang, ACS Nano, 2010, 4, 1799.
- 21 M. Pumera, Nanoscale, 2010, 2, 1643.
- 22 T. Mirkovic, N. S. Zacharia, G. D. Scholes and G. A. Ozin, *Small*, 2010, 6, 159.
- 23 W. Gao, S. Sattayasamitsathit, J. Orozco and J. Wang, J. Am. Chem. Soc., 2011, 133, 11862.
- 24 D. Kagan, S. Campuzano, S. Balasubramanian, F. Kuralay, G. Flechsig and J. Wang, *Nano Lett.*, 2011, 11, 2083.
- 25 P. Fischer and A. Ghosh, Nanoscale, 2011, 3, 557.
- 26 J. Gibbs and Y. Zhao, Front. Mater. Sci., 2011, 5, 25.
- 27 L. Baraban, D. Makarov, R. Streubel, I. Mönch,
  D. Grimm, S. Sanchez and O. G. Schmidt, ACS Nano,
  2012, 6, 3383.
- 28 L. Soler and S. Sánchez, Nanoscale, 2014, 6, 7175.
- 29 W. Gao, R. F. Dong, S. Thamphiwatana, J. X. Li, W. W. Gao, L. F. Zhang and J. Wang, ACS Nano, 2015, 9, 117.
- 30 M. Guix, J. Orozco, M. García, W. Gao, S. Sattayasamitsathit, A. Merkoçi, A. Escarpa and J. Wang, *ACS Nano*, 2012, 6, 4445.

- 31 M. García, J. Orozco, M. Guix, W. Gao, S. Sattayasamitsathit, A. Escarpa, A. Merkoçi and J. Wang, *Nanoscale*, 2013, 5, 1325.
- 32 O. G. Schmidt and K. Eberl, Nature, 2001, 410, 168.
- 33 Y. F. Mei, G. S. Huang, A. A. Solovev, E. B. Ureña, I. Mönch,
   F. Ding, T. Reindl, R. K. Y. Fu, P. K. Chu and O. G. Schmidt,
   *Adv. Mater.*, 2008, 20, 4085.
- 34 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103.
- 35 N. Chandrasekharan, P. V. Kamat, J. Hu and G. Jones, *J. Phys. Chem. B*, 2000, **104**, 11103.
- 36 Y. Yin, T. Qiu, L. Ma, X. Z. Lang, Y. Zhang, G. S. Huang, Y. F. Mei and O. G. Schmidt, *J. Phys. Chem. C*, 2012, **116**, 25504.
- 37 A. A. Solovev, Y. F. Mei, E. B. Ureña, G. S. Huang and O. G. Schmidt, *Small*, 2009, 5, 1688.
- 38 T. Qiu, W. J. Zhang, X. Z. Lang, Y. J. Zhou, T. J. Cui and P. K. Chu, *Small*, 2009, **5**, 2333.
- 39 W. Gao, A. Uygun and J. Wang, J. Am. Chem. Soc., 2012, 134, 897.
- 40 W. Gao, X. M. Feng, A. Pei, Y. Gu, J. X. Li and J. Wang, *Nanoscale*, 2013, 5, 4696.