Self-propelled supramolecular nanomotors with temperature-responsive speed regulation

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1. Materials

Unless stated otherwise, all reagents and chemicals were used without further purification. Styrene (Sigma-Aldrich) was distilled before polymerization to remove the inhibitor. N-isopropyl acrylamide from Sigma-Aldrich was purified by repeated recrystallization in a mixture of toluene/hexane (50:50, v/v). CuBr (Sigma-Aldrich) for ATRP was washed with acetic acid and followed by methanol (MeOH) for three times and protected under Ar. Tetrahydrofuran (THF) for reaction was distilled under Argon from sodium/benzophenone. Ultra pure MilliQ water obtained with MilliQ QPOD purification system (18.2 MΩ) was used for self-assembly and dialysis of polymersomes/stomatocytes. Spectra/Por® Dialysis Membrane MWCO: 12-14,000 g/mol was used for dialysis of polymersomes/stomatocytes. Polyvinyl pyrrolidone (PVP, Mn 10 kg/mol), poly(ethylene glycol) methyl ether (Mn 2 kg/mol), α-ω-amino-poly(ethylene glycol) (Mn 2 kg/mol), L (+) ascorbic acid, magnesium sulfate, sodium bicarbonate, potassium tetrachloroplatinate (II), sodium chloride, ethylenediaminetetraacetic acid (EDTA), 1-phenyl-1-trimethylsiloxyethene, α-bromoisobutyryl bromide, (Benzotriazol-1-1-oxy)tripyrrolidinophosphonium hexafluorophosphate (PyBOP), chloroform-d (CDCl3), methanol-d4 (MeOD), tert-butyl α-bromoisobutyrate, N,N,N’,N”-Pentamethyldiethylenetriamine (PMDETA), dimethylformamide (DMF) and 3,3’,5,5’-tetramethylbenzidine (TMB) were purchased from Sigma-Aldrich. THF, anisole and N,N-Diisopropylethylamine (DIPEA) were obtained from Acros. MeOH, hydrochloric acid (37%), triethylamine and hydrogen peroxide were purchased from J.T. Baker. Diethyl ether (Carlo erba Reagents), 1,4-dioxane (Biosolve BV), dichloromethane (CH2Cl2, Fisher Chemical) and Nile red (Chem Impex) were also used.

2. Instruments

Routine NMR spectra were recorded on a Varian Inova 400 spectrometer with CDCl3 as a solvent. Diffusion measurements were performed at 298 K on a Bruker Avance III 500 MHz spectrometer equipped with a BBFO probe. The maximum z-gradient for the probe is 53.5 G/cm. Diffusion measurements were calibrated to pure methanol and ethylene glycol. The pulse sequence incorporated delays for eddy currents to dissipate and bipolar gradients for encoding and decoding diffusion information. Malvern Zetasizer Nano S was used for Dynamic light scattering (DLS) analysis with following settings: temperature 25 °C, He-Ne laser wavelength 633 nm and detector angle 170°. For transmission electron microscopy, a JEOL 1010 Transmission Electron Microscope with MegaView Soft Imaging camera at an acceleration voltage of 60 kV was used. Cryogenic transmission microscopy was performed on a JEOL TEM 2100 with high-quality Gatan 895 ultrascan 4000 bottom mount camera (4080x4080 pixels). Energy-dispersive X-ray element mapping was done on a Bruker Quantax EDS system with an STEM detector incorporated. Nanoparticles tracking analysis (NTA) of stomatocytes nanomotors was performed on NanoSight NS500.
3. Synthetic procedures, self-assembly and characterizations

Scheme 1 Synthetic route for the block copolymer poly(ethylene glycol)-b-polystyrene (PEG-b-PS) and α-bromo ester functional-poly(ethylene glycol)-b-polystyrene (Br-PEG-b-PS) via ATRP protocol.

3.1. Synthesis of α-Methoxy-poly(ethylene glycol)₄₄ ATRP macromolecular initiator (1)

Poly(ethylene glycol) methyl ether (5.00 g, 2.50 mmol) was dried by co-evaporation with toluene. The polymer was dissolved in freshly distilled THF in a flame-dried Schlenk flask. After adding triethylamine (1.04 mL, 7.50 mmol), the mixture was cooled to 0 °C. α-bromoisobutyryl bromide (616 µL, 5.00 mmol) was added dropwise. After addition, the resulting solution was stirred for 24h while slowly warming to room temperature. After the reaction, the white precipitate was filtered off and the solution was concentrated. The polymer was precipitated in ice-cold diethyl ether (2x). The polymer was characterized by ¹H-NMR in CDCl₃. (Supplementary Figure 1)

¹H-NMR (400 MHz, CDCl₃) δ: 4.33 (t, 2H, CH₂CH₂OC(O)C(CH₃)₂Br), 3.76 (t, 2H, CH₂CH₂OC(O)C(CH₃)₂Br), 3.65 (br. s, PEG backbone), 3.55 (m, 2H, CH₃OCH₂), 3.38 (s, 3H, CH₃OCH₂), 1.94 (s, 6H, C(CH₃)₂Br) ppm.

3.2. Synthesis of poly(ethylene glycol)-b-polystyrene (2)

The Schlenk tube with CuBr (45 mg, 0.32 mmol) was evacuated for 15 min and refilled with Ar for three times. PMDETA (66 µL, 0.32 mmol) in anisole (0.5 mL) was added, followed by 15 min vigorously stirring. Styrene (5 mL, 43.6 mmol) in anisole (0.5 mL) was added via a syringe and degased for 15 min. After cooling the mixture to 0 °C, PEG-initiator (215 mg, 0.1 mmol) dissolved in anisole (0.5 mL) was injected and the solution was degassed for another 15 min. The Schlenk tube was transferred into an oil bath at 90 °C. ¹H-NMR was used for monitoring the reaction process. Upon attainment of the required molecular weight, 1-phenyl-1-trimethylsiloxethene
The final polymer was characterized by the organic layer was collected and dried overnight. The polymer was obtained after precipitation in MeOH (3x) and dried under vacuum overnight. The polymer was characterized by \(^1\)H-NMR in CDCl₃. (Supplementary Figure 2)

\(^1\)H-NMR (400 MHz, CDCl₃) δ: 7.20-6.30 (br. s, PS arom.), 3.64 (br. s, PEG backbone), 3.38 (s, 3H, CH₂OCH₂), 2.30-1.20 (br. s, PS backbone), 0.90 (br. m, 6H, C(O)C(CH₃)₂CH₂) ppm.

3.3. Synthesis of α-tert-Butyloxycarbonyl-polystyrene (3)

The Schlenk tube with CuBr (45 mg, 0.32 mmol) was evacuated for 15 min and refilled with Ar for three times. PMDETA (66 µL, 0.32 mmol) in anisole (0.5 mL) was added, followed by 15 min vigorously stirring. Styrene (5.74 mL, 50 mmol) in anisole (0.5 mL) was added via a syringe and degassed for 15 min. After cooling the mixture to 0 °C, tert-butyl α-bromoisobutyrate (27 µL, 0.14 mmol) in anisole was injected and the solution was degassed for another 15 min. The Schlenk tube was transferred into an oil bath at 90 °C. \(^1\)H-NMR was used for monitoring the reaction process. Upon attainment of the required molecular weight, the reaction was terminated by adding 1-phenyl-1-trimethylsiloxyethene (1.91 mL, 9.28 mmol). The mixture was stirred for 2 h. The solution was diluted with CH₂Cl₂ and extracted with an aqueous solution of EDTA (65 mM). The organic layer was collected and dried with MgSO₄ and concentrated. The polymer was obtained after precipitation in MeOH (3x) and dried under vacuum overnight. The polymer was characterized by \(^1\)H-NMR in CDCl₃. (Supplementary Figure 3)

\(^1\)H-NMR (400 MHz, CDCl₃) δ: 7.20-6.30 (br. s, PS arom.), 2.30-1.20 (br. s, PS backbone), 1.25 (br. m, 9H, C(CH₃)₃), 0.92 (br. m, 6H, C(O)C(CH₃)₂CH₂) ppm.

3.4. Synthesis of α-Carboxylic acid-polystyrene (4)

Polymer 3 (3 g) was dissolved in 1,4-dioxane (30 mL) and concentrated HCl (1.5 mL, 37%) was added. The reaction was refluxed at 110 °C overnight. The mixture was dried using a rotary evaporator and then dissolved in CH₂Cl₂. The polymer was obtained after precipitation in MeOH (3x) and then dried under vacuum overnight. The polymer was characterized by \(^1\)H-NMR in CDCl₃. (Supplementary Figure 4)

\(^1\)H-NMR (400 MHz, CDCl₃) δ: 7.20-6.30 (br. s, PS arom.), 2.30-1.20 (br. s, PS backbone), 0.96 (br. m, 6H, C(O)C(CH₃)₂CH₂) ppm.

3.5. Synthesis of α-amino-poly(ethylene glycol)-b-polystyrene (5)

Polymer 4 (1 g, 43.5 µmol), α-ω-amino-poly(ethylene glycol) (521.7 mg, 260 µmol) and DIPEA (17.4 µL, 100 µmol) were dissolved in DMF (12 mL). The solution was cooled to 0 °C and PyBOP (42 mg, 80 µmol) was added. The reaction was stirred overnight, while slowly warming to room temperature. The progress of the coupling was monitored by GPC. (Supplementary Figure 5, 6) After that, the mixture was diluted with CH₂Cl₂ and extracted with NaHCO₃ solution (4 wt%) and saturated NaCl solution. The organic layer was collected and dried with MgSO₄ and concentrated. The polymer was obtained after precipitation in MeOH (3x) and dried under vacuum overnight. The final polymer was characterized by \(^1\)H-NMR in CDCl₃. (Supplementary Figure 7)

\(^1\)H-NMR (400 MHz, CDCl₃) δ: 7.20-6.30 (br. s, PS arom.), 3.64 (br. s, PEG backbone), 2.30-1.20 (br.
3.6. Synthesis of polystyrene-b-poly(ethylene glycol)-ω-bromoisobutyramide (6)

Polymer S (500 mg, 20 μmol) was dissolved in 15 ml freshly distilled THF in a flame-dried Schlenk tube. After adding TEA (104 μL, 750 μmol), the mixture was cooled to 0 °C. α-bromoisobutyryl bromide (61.6 μL, 500 μmol) was added dropwise. After addition, the resulting solution was stirred for 24 h while slowly warming to room temperature. After the reaction, the white precipitate was filtered off and the solution was concentrated. The polymer was precipitated in ice-cold MeOH(3x). The polymer was characterized by 1H-NMR in CDCl3. (Supplementary Figure 8)

1H-NMR (400 MHZ, CDCl3) δ: 7.20-6.30 (br. s, PS arom.), 3.64 (br. s, PEG backbone), 2.30-1.20 (br. s, PS backbone), 1.96 (s, 6H, C(CH3)2Br), 0.90 (br. m, 6H, C(O)C(CH3)2CH2) ppm. ω

3.7. Heteronuclear Multiple Bond Correlation (HMBC) measurement

The HMBC experiment measured correlations between carbons and protons that are separated by two, three, and, sometimes in conjugated systems, four bonds. In order to confirm Br was covalent attached to polymer, 5 mg Br-PEG-b-PS/α-bromoisobutryl bromide was fully dissolved in 0.5 mL CDCl3 and measured by HMBC respectively. The HMBC experiment was performed with 2-fold J-filter set to 120 Hz and 170 Hz and optimized for a 10 Hz long-range C-H coupling. The experiment was performed under constant time in order to minimize the effect of relaxation. The size acquired was 2048x256 and then processed with zero-filling to 4096x512. After measurement, the difference between the HMBC signal of correlation from Br-PEG-b-PS and that of α-bromoisobutryl bromide was compared in Supplementary Figure 9.

3.8. Preparation of PtNPs with PVP coating

4 mL K2PtCl4 solution (20 mM) was added into 40 mg PVP, followed by 48 hours stirring. After that, 35 mg L (+) ascorbic acid in 1 mL of MilliQ water was added into the solution. The resulting solution was sonicated (VWR Ultrasonic Cleaner Model 75D) at room temperature for 1 h. The PtNPs were characterized by TEM. (Supplementary Figure 10)

3.9. Self-assembly of Stoma or Stoma-Br

10 mg PEG-b-PS (or 9 mg PEG-b-PS and 1mg Br-PEG-b-PS) was fully dissolved in 1 mL mixture of THF/dioxane (4:1, v/v). 1 mL of MilliQ water was slowly added into the solution by a syringe pump at a rate of 1 mL/h. After vigorous dialysis for at least 48 hours, Stoma/Stoma-Br was obtained.

3.10. Self-assembly of PtNPs-Stoma or PtNPs-Stoma-Br

10 mg PEG-b-PS (or 9 mg PEG-b-PS and 1mg Br-PEG-b-PS) was fully dissolved in 1 mL mixture of THF/dioxane (4:1, v/v). 0.35 mL of MilliQ water was slowly added by a syringe pump at a rate of 1 mL/h, followed by addition of preformed PtNPs solution (0.65 mL) also at a rate of 1 mL/h. After dialysis for at least 48 hours, PtNPs-Stoma or PtNPs-Stoma-Br was obtained.

3.11. Size change after growing PNIPAM brushes
The sizes and size distributions of PtNPs-Stoma, PtNPs-Stoma-Br, PtNPs-Stoma and PtNPs-Stoma-Br after SI-ATRP (PtNPs-Stoma without Br after SI-ATRP as a control) were measured respectively by Malvern DLS-Zetasizer. (Supplementary Table 1)

3.12. NMR Calculation for Molecular Weight of PNIPAM Brush

In order to calculate the length of PNIPAM brushes, the sample of Stoma-Brush was freeze-dried and re-dissolved in CDCl₃ for ¹H-NMR measurement (Supplementary Figure 11). The molecular weight of PNIPAM was calculated according to the NMR integration. ¹H-NMR (400 MHz, CDCl₃) δ: 7.20-6.30 (br. s, PS arom.), 4.00 (br. s, PNIPAM, NHCH(CH₃)₂), 3.64 (br. s, PEG backbone), 2.30-1.20 (br. s, PS backbone), 1.14 (br. s, PNIPAM, NHCH(CH₃)₂) ppm.

3.13. Stability of stomatocytes in methanol

In order to check the stability of stomatocytes in MeOH, the sample was suspended in MeOH. TEM samples were then made and analyzed. (Supplementary Figure 12)

3.14. Diffusion NMR Measurements

Bruker DMX 500 MHz NMR was used for Diffusion NMR measurements. Diffusion NMR experiments resolve different compounds spectroscopically in a mixture based on their differing diffusion coefficients, depending on the size and shape of the molecules. Free PNIPAM with different molecule weight, Stoma mixed with PNIPAM and Stoma-Brush in MeOD were measured respectively and diffusion coefficients were calculated according to the equation B+exp(-x*F) (Mono-exponential Fit). (Supplementary Figure 13)

3.15. FT-IR Measurements

Bruker TENSOR 27 was used for IR measurements. Empty Stoma, Stoma-Br, Stoma without Br modification after SI-ATRP and Stoma-Brush solution were measured respectively. (Supplementary Figure 14)

3.16. Mixing Stoma and Stoma-Brush with Nile Red

To demonstrate that a collapsed hydrophobic layer was formed around the stomatocyte when the particles were heated above the LCST of PNIPAM the hydrophobic dye Nile red was used. Nile red is almost non-fluorescent in water but undergoes fluorescence enhancement and large absorption and emission blue shifts in hydrophobic environments.

5 μL Nile red in DMF (6 mg/mL) was mixed with 100 μL Stoma-Brush (3.8 x10¹¹ particles/mL, measured by Nanosight) and also with normal Stoma (3.9 x10¹¹ particles/mL, measured by Nanosight, almost same concentration with Stoma-Brush) respectively, and the fluorescent intensities of both samples were measured at 30 °C by fluorescence spectrometer (Perkin Elmer LS53). The intensities were also measured when the whole system was heated to 40 °C (cross the LCST of PNIPAM). After cooling the system back to 30 °C, the intensities of both samples were measured again. (Supplementary Figure 15)

3.17. Movement Analysis

Nanosight NS500 was used for the measurements of motion of stomatocytes nanomotors.
PtNPs-Stoma without H$_2$O$_2$ fuel, PtNPs-Stoma with H$_2$O$_2$, PtNPs-Stoma-Brush without H$_2$O$_2$ and PtNPs-Stoma-Brush with H$_2$O$_2$ were measured respectively. The fitting of the MSD allows for calculation of the speed of the nanomotors by using the self-diffusiophoretic model proposed by Golestanian and coworkers. While a purely diffusive system would show only a linear component according to \((4D)\Delta t\) equation from which an enhanced diffusion coefficient can be extracted, our MSD curves are not linear and show a parabolic fit according to the equation \((4D)\Delta t + (v^2)(\Delta t^3)\) from which we can extract the velocity of the particles. Chemotaxis and Migration Tool 2.0 from Ibidi Company was used for directionality calculation. Mean square displacement (MSD), directionality and MSD fitting can be seen in Supplementary Figure 16 and Supplementary Figure 17.

\[
\text{Directionality} = \frac{1}{n} \sum_{i=1}^{n} d_i = \frac{1}{n} \sum_{i=1}^{n} d_i^{\text{euclid}} / d_i^{\text{accum}}
\]

### 3.18. Catalytic Efficiency of PtNPs

In order to figure out the reason of PtNPs-Stoma-Brush move faster after one cycle, catalytic efficiency of PtNPs was measured via 3,3’,5,5’-tetramethylbenzidine (TMB)-H$_2$O$_2$ reaction. PtNPs are shown to have activity that can be monitored colorimetrically by the color change seen from the oxidation of TMB to its one-electron oxidation product. 50 µL TMB (dissolved in DMSO, 4 mg/mL) and 50 µL H$_2$O$_2$ solution (5%) were added into 900 µL citric buffer (pH=4.0) as working solution. 10 µL PtNPs solution/PtNPs solution after one cycle/PtNPs solution after two cycles/PtNPs solution after three cycles was added respectively into 240 µL working solution and UV absorbance was measured afterwards, which was related to catalytic efficiency of PtNPs. The absorbances of samples were compared in Supplementary Figure 19.

### 4. Supplementary Figures and Tables

Supplementary Figure 1. $^1$H-NMR spectrum of α-Methoxy-poly(ethylene glycol) initiator.
Supplementary Figure 2. $^1$H-NMR spectrum of poly(ethylene glycol)-b-polystyrene. According to integration of NMR spectrum, the length of PS was 212 (PEG$_{44}$-b-PS$_{212}$). PDI of PEG$_{44}$-b-PS$_{212}$ was 1.07 according to GPC.

Supplementary Figure 3. $^1$H-NMR spectrum of $\alpha$-tert-Butyloxy carbonyl-polystyrene. From the NMR spectrum, the specific resonance of the tert-butyl group (1.25 ppm) was observed, which confirmed that $\alpha$-tert-Butyloxy carbonyl-polystyrene was synthesized.
Supplementary Figure 4. $^1$H-NMR spectrum of $\alpha$-Carboxylic acid-polystyrene. After deprotection, the peak of the tert-butyl group disappeared in the NMR spectrum.

Supplementary Figure 5. GPC measurement of coupling at 0h. According to GPC data, number average molecular weight (Mn) was 14473 Da and weight average molecular weight (Mw) was 15357 Da. (PDI=1.06)

Supplementary Figure 6. GPC measurement of coupling at 96h. After 4 days, the peak of polymer was shifted from 9.931 min to 9.794 min. Compared to the molecular weight at 0h, Mn was increased from 14473 Da to 18061 Da and Mw was increased from 15357 to 18941 Da (PDI=1.04), which indicated that the coupling reaction was happened.
Supplementary Figure 7. $^1$H-NMR spectrum of $\alpha$-amino-poly(ethylene glycol)-$b$-polystyrene.

Supplementary Figure 8. $^1$H-NMR of polystyrene-$b$-poly(ethylene glycol)-$\omega$-bromoisobutyramide. Specific peak around 1.96 ppm of two methyl groups was observed from NMR spectrum, confirmed that bromide was attached to the polymer. According to NMR integration, the length of PS was 238 (Br-PEG$_{44}$-$b$-PS$_{238}$). The PDI of Br-PEG$_{44}$-$b$-PS$_{238}$ was 1.20 according to GPC.
Supplementary Figure 9. Characterization of functional polymer Br-PEG-b-PS. Comparison of HMBC signal of Br-PEG-b-PS (red) with that of α-bromoisobutyryl bromide (green). As shown in Supplementary Figure 9, the Heteronuclear Multiple Bond Correlation (HMBC) signal of the methyl group (1) from Br-PEG-b-PS (red) correlated with the other methyl group (3, δ_{13C}=32.50 ppm), the quaternary carbon (2, δ_{13C}=62.90 ppm) and the neighboring carbonyl group (4, δ_{13C}=172.27 ppm). The significant shift of the signals compared to that of non-conjugated α-bromoisobutyryl bromide (green, δ_{13C}=30.95 ppm, 65.99 ppm and 170.64 ppm respectively), confirmed the successful attachment of the ATRP initiator onto the polymer.

Supplementary Figure 10. TEM image of PtNPs.
Supplementary Figure 11. $^1$H-NMR spectrum of Stoma-Brush. From the $^1$H-NMR spectrum, specific PNIPAM peaks at 1.14 ppm and 4.00 ppm were observed. After integrating the ratio between PNIPAM and PS part, the molecular weight of PNIPAM was 85.5 kg/mol, so the length of PNIPAM brushes was 769.

Supplementary Figure 12. a) TEM image of stomatocytes in water; b) TEM image of stomatocytes in MeOH. (Scale bar: 500 nm) From the TEM figures, no morphological changes were observed which indicated the stability of stomatocytes in MeOH.
Supplementary Figure 13. Diffusion NMR. a) Diffusion NMR of free PNIPAM (100k) in MeOD; b) Fitting curve of diffusion coefficient of free PNIPAM (100k); c) Diffusion NMR of mixture of Stoma and free PNIPAM (23k) in MeOD; d) Fitting curve of diffusion coefficient of mixture of Stoma and free PNIPAM (23k). PNIPAM peaks at around 1.2 ppm and 4.0 ppm were observed from NMR spectrum. After fitting with the equation (Mono-exponential Fit, \( B + \exp(-x*F) \)), \( D_Y \) (diffusion coefficient from PNIPAM at 1.2 ppm) and \( D_{Y1} \) (diffusion coefficient from PNIPAM at 4.0 ppm) were obtained. \( D_{Y,Y1} \) was the average of \( D_Y \) and \( D_{Y1} \). \( D_{Y2} \) was the diffusion coefficient from MeOD at 3.3 ppm. The diffusion coefficient of MeOD was much lower than that of PNIPAM as expected. The diffusion coefficients of MeOD obtained from different measurements were almost the same, which indicated nice repeatability of diffusion NMR.

Supplementary Figure 14. FT-IR spectrums of empty Stoma, Stoma-Br, Stoma after SI-ATRP and Stoma-Brush. PNIPAM peaks were observed only after SI-ATRP of Stoma-Br.
Supplementary Figure 15. Mixing Stoma and Stoma-Brush with hydrophobic Nile red at different temperatures.

Supplementary Figure 16. Average MSD and MSD fitting of PtNPs-Stoma-Brush in the presence of Hydrogen peroxide fuel. “Δt” is not the total time of the video recording and particle monitoring but instead the time difference used for measuring the deviation over time between the position of the particle and the reference position, which is typically plotted in a MSD graph. The velocity of a directed motion was extracted from the fitting of the MSD curve by using the equation \((4D)\Delta t + (v^2)(\Delta t^2)\) while for a Brownian motion, the MSD show only a linear fitting according to the equation \((4D)\Delta t\).
Supplementary Figure 17. MSD and directionality of stomatocyte nanomotors. a) MSD of PtNPs-Stoma-Brush without H₂O₂; b) MSD of PtNPs-Stoma without H₂O₂; c) MSD of PtNPs-Stoma with H₂O₂; d) directionality of PtNPs-Stoma-Brush without H₂O₂, PtNPs-Stoma with H₂O₂ and PtNPs-Stoma without H₂O₂. The directionality was calculated by comparing the Euclidian distance to the Accumulated distance, which represented a measurement of the directness of trajectories. Software Chemotaxis and Migration Tool 2.0 from Ibidi Company was used for directionality calculation.

Supplementary Figure 18. Bubble observation. a-j) 1µL PtNPs (1) or PtNPs-Stoma (2) was added into 1 mL H₂O₂ solution (4.98 mM, same concentration with the motion measurements). From the these photos, no visible bubbles can be observed; k) 30 µL PtNPs was added into 1 mL 5% H₂O₂ solution. A lot of bubbles were observed; j) 30 µL PtNPs was added into 1 mL 0.5% H₂O₂ solution. Few bubbles were observed.
Supplementary Figure 19. Catalytic efficiency of PtNPs solution after cycles. The catalytic efficiency of PtNPs increased after cycles.

Supplementary Figure 20. The velocity of PtNPs-Stoma-Brush in time. The velocity of motors were calculated according to MSDs fitting by the equation $(4D)\Delta t + (v^2)(\Delta t^2)$.

Supplementary Table 1. Size of Stomatocyte and Stomatocyte after growing brush

<table>
<thead>
<tr>
<th></th>
<th>Before growing brush/nm</th>
<th>After growing brush/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% PtNPs-Stoma-Br</td>
<td>337 (PDI=0.150)</td>
<td>434 (PDI=0.062)</td>
</tr>
<tr>
<td>10% PtNPs-Stoma-Br</td>
<td>341 (PDI=0.177)</td>
<td>689 (PDI=0.060)</td>
</tr>
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</table>
Supplementary Table 2. Size of PtNPs-Stoma-Brush in PBS and water

<table>
<thead>
<tr>
<th></th>
<th>PBS/nm</th>
<th>Water/nm</th>
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<tbody>
<tr>
<td>PtNPs-Stoma-Brush</td>
<td>678.7 (PDI=0.074)</td>
<td>680.1 (PDI=0.107)</td>
</tr>
</tbody>
</table>