Electronic Supplementary Information (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2015

Efficient polymeric micromotor doped with Pt nanoparticle@carbon nanotube for complex bio-media†

Yana Li, Jie Wu,* Yuzhe Xie, and Huangxian Ju

State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P.R. China

Experimental

Materials and reagents. Aniline and pyrrole monomers were purchased from Alfa Aesar China Ltd. Sodium cholate hydrate (Nach), 3,4-ethylenedioxythiophene (EDOT), poly(diallyldimethylammonium chloride) (PDDA, MW ~70000), poly(sodium 4-styrenesulfonate) (PSS, MW ~70000, powder), bovine serum albumin (BSA), Dulbecco's Modified Eagle's medium (DMEM) and wheat germ agglutinin (WGA) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Commercial multiwall carbon nanotubes (CNTs, diameters 20-40 nm, purity>97%) were purchased from Shenzhen Nanotech Port Co., Ltd. (China). Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was obtained from Shanghai Reagent Co. (China). The clinical human serum samples were from Jiangsu Cancer Hospital (China). Luria-Bertani broth (Product Code: CM 158) was purchased from Beijing Land Bridge Technology Co., Ltd. (China). Bacterial strains of *E. coli* (ATCC 25922) were purchased from Huankai Microbial Technology Co., Ltd. (China), which were grown in Luria-Bertani broth at 37 ºC with shaking

(180 rpm) to an OD600 of ~0.6 prior to use. Phosphate-buffered saline (PBS, 0.01 M, pH 9.0) was used as coupling buffer for the immobilization of WGA. Washing buffer was 0.01 M PBS (pH 7.4) spiked with 0.05% Tween-20. Blocking buffer, which was used to block the residual reactive sites on the WGA-modified micromotor, was 0.01 M PBS (pH 7.4) containing 5% BSA. Other reagents were of analytical grade and used as received. Ultrapure water obtained from a Millipore water purification system (≥18 MΩ, Milli-Q, Millipore) was used in all experiments.

Apparatus. Template-assisted electrochemical growth of polymers was carried out with a CHI 660B electrochemical workstation (CH Instruments Inc., USA). The morphology of the micromotors was examined with scanning electron microscope (SEM) (Hitachi S-4800, Japan) and transmission electron microscope (TEM) (JEM-2100, JEOL, Japan). The images and videos were captured by Leica DMI 3000B inverted microscope equipped with a Photometrics Evolve 512/SC camera (Roper Scientific, Duluth, GA), and acquired at a frame rate of 10 frames/s using the Leica MM AF 1.5 software.

Synthesis of PtNP@CNT. Pt nanoparticles (PtNPs) with a size of ~2 nm were synthesized using sodium citrate as reductant. Briefly, after 200 mL of 0.1 mg mL^{-1} H_2PtCl_6 was brought to boil, 5 mL of 38 mM sodium citrate was rapidly added with vigorous stirring, which led to a color change from pale yellow to brownness. The mixture was boiled for 10 min and then stirred for additional 30 min. After the mixture reached room temperature, it was filtered through a 0.2 μm membrane filter to obtain PtNPs.

CNTs were firstly refluxed in a mixed acid (sulfuric acid : nitric acid = 3:1) at 60 °C for 12 h.[S1] After washed repeatedly with water until pH 7.0 and dried at 60 °C, the CNTs were dispersed in 1 M NaOH to introduce negative charges on their surface. After washed with water,

the negatively charged CNTs were dispersed in 2 mg mL^{-1} PDDA to adsorb the positively charged polycation, and then mixed with negatively charged PtNPs to obtain PtNP@CNT.

Preparation of micromotors. The polymeric PEDOT/PtNP@CNT-PPy micromotors were prepared with a template-directed electrodeposition protocol.[S2] Briefly, a polycarbonate membrane, containing 5 μm-diameter micropores (Catalog No 7060-2513, Whatman, U.S.A), was employed as the template. A gold film with a thickness of 75 nm was firstly sputtered on one side of the porous membrane to serve as working electrode. A Pt wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The membrane was then assembled in a plating cell with an aluminum foil serving as contact. On the inner wall of the micropores PEDOT outer layer was electropolymerized at +0.80 V to a charge of 0.30 C in a plating solution containing 15 mM EDOT, 7.5 mM KNO_3 and 100 mM sodium dodecyl sulfate (SDS). Then, 200 μg mL^{-1} dispersion of PtNP@CNT was filled into the micropores, followed by electrochemical plating at +0.80 V in a solution containing 37 mM pyrrole and 7.5 mM KNO_3 to a charge of 0.10 C to form PtNP@CNT-PPy inner layer. Finally, the template was dissolved in methylene chloride for 15 min to release the PEDOT/PtNP@CNT-PPy micromotors, which were collected by centrifugation and washed repeatedly with methylene chloride, ethanol and ultrapure water, respectively. The micromotors were finally collected and stored in ultrapure water at room temperature.

The Fe_3O_4 nanoparticles dopped micromotor (PEDOT/PtNP@CNT-Fe_3O_4-PPy), PEDOT/PtNP-PPy or PEDOT/CNT-PPy micromotor was prepared according to the similar procedure by replacing the PtNP@CNT dispersion with the mixture of 200 μg mL^{-1} PtNP@CNT and 50 μg mL^{-1} Fe_3O_4 nanoparticles, 200 μg mL^{-1} PtNPs or CNTs. Here, Fe_3O_4 nanoparticles were prepared following the precudure reported previously.[S3] Briefly, 1 g $FeCl_3 \cdot 6H_2O$, 2 g

anhydrous sodium acetate and 6.5 g 1,6-hexanediamine were dissolved into 30 mL ethylene glycol and stirred until transparency. Next, the mixture was transferred into the microwave system and treated at 200 ºC for 30 min. Then, it was washed with ethanol and water, separated by a permanent magnet and finally redispersed in de-ionized water for further use.

As control, the PEDOT/Pt bilayer micromotors were prepared by galvanostatically depositing inner Pt layer on PEDOT outer layer at –2 mA for 1 h in a solution containing 18 mM H_2PtCl_6 and 0.05 M HCl, and then dissolving the template with methylene chloride.

Fabrication of WGA modified PEDOT/PtNP@CNT-PPy micromotors. The PEDOT/PtNP@CNT-PPy micromotors were sequentially incubated with PSS and PDDA (0.1 mg mL^{-1}) for 30 min, and then underwent centrifugation with ultrapure water to remove excess polyelectrolyte. Next, citrate wrapped AuNPs with 13 nm diameter[S4] were added to the polyelectrolyte functionalized micromotors under vigorous stirring for 1 h at room temperature. The unattached AuNPs were isolated by centrifugation (6000 rpm) with ultrapure water and the obtained AuNP/PEDOT/PtNP@CNT-PPy micromotors were dispersed in coupling buffer. Subsequently, WGA (200 μg mL^{-1}) was added into the suspension to incubate at room temperature with gentle shaking for 2 h. Afterward, the micromotors were collected by centrifugation and dispersed in blocking buffer for 1 h to block the free surface of AuNPs. After washing with washing buffer, the WGA modified micromotors were stored in PBS (10 mM, pH 7.4) at 4 °C.

Supporting video captions

Video S1. Autonomous motion of PEDOT/PtNP@CNT-PANI, PEDOT/PtNP@CNT-PEDOT, PEDOT/PtNP@CNT-PPy micromotors in 5% H_2O_2 containing 1.6% (w/v) sodium cholate.

Video S2. Autonomous motion of PEDOT/PtNP@CNT-PPy micromotor in 1% to 15% H_2O_2 containing 1.6% (w/v) sodium cholate.

Video S3. Autonomous motion of PEDOT/PtNP-PPy, PEDOT/CNT-PPy, PEDOT/PtNP@CNT-PPy micromotors in 2% H_2O_2 containing 1.6% (w/v) sodium cholate.

Video S4. Magnetic guidance of PEDOT/PtNP@CNT-Fe_3O_4-PPy micromotor in 2% H_2O_2 containing 1.6% (w/v) sodium cholate by applying a magnetic field to follow the predetermined (N, J, U) trajectories**.**

Video S5. Autonomous motion of PEDOT/Pt and PEDOT/PtNP@CNT-PPy micromotors in 2% H_2O_2 containing 1.6% (w/v) sodium cholate and 0 to 1000 μM BSA.

Video S6. Autonomous motion of PEDOT/PtNP@CNT-PPy micromotors in water, 0.1 M KCl solution, human serum and cell culture medium in the presence of 2% H_2O_2 and 1.6% (w/v) sodium cholate.

Video S7. Autonomous motion of WGA-modified micromotor in 0.01 M PBS (pH 7.4), and bare and WGA-modified micromotors in Luria-Bertani broth containing 1.8×10^5 cfu *E. coli* after navigation for 3 min in the presence of 2% H_2O_2 and 1.6% (w/v) sodium cholate.

Supporting figures

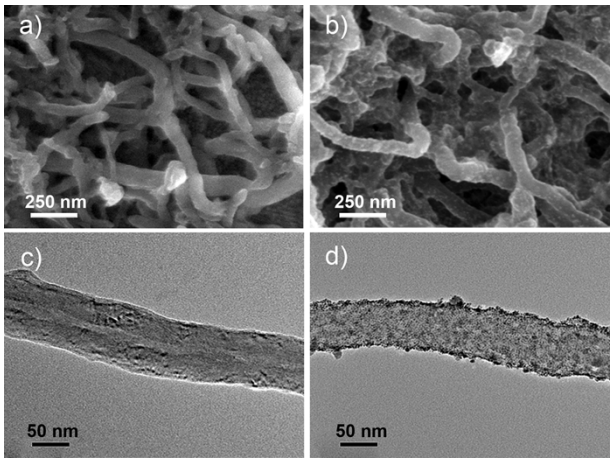

Fig. S1. SEM and TEM images of bare CNT (a, c) and PtNP@CNT (b, d).

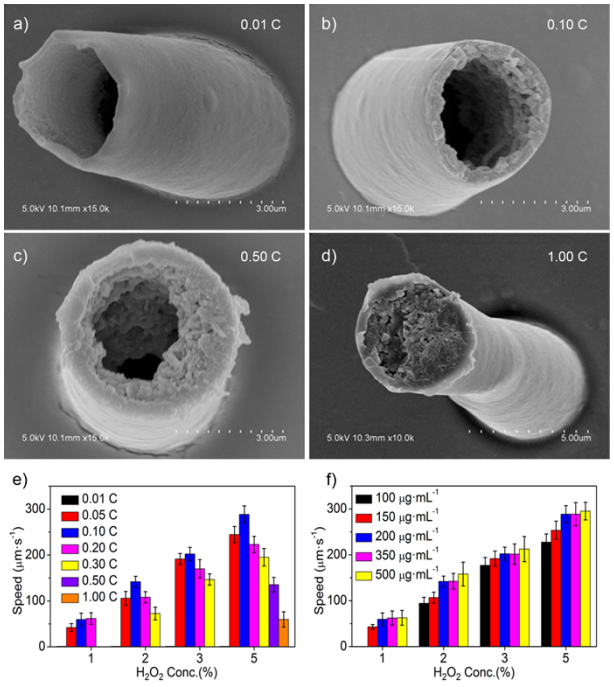

Fig. S2. SEM images of PEDOT/PtNP@CNT-PPy micromotors prepared with a) 0.01, b) 0.10, c) 0.50 and d) 1.00 C for the inner layer, and dependence of motion speed in H_2O_2 solutions containing 1.6% (w/v) sodium cholate on e) deposition charge and f) concentration of PtNP@CNT. Error bars represented the standard deviations of speeds from 20 micromotors.

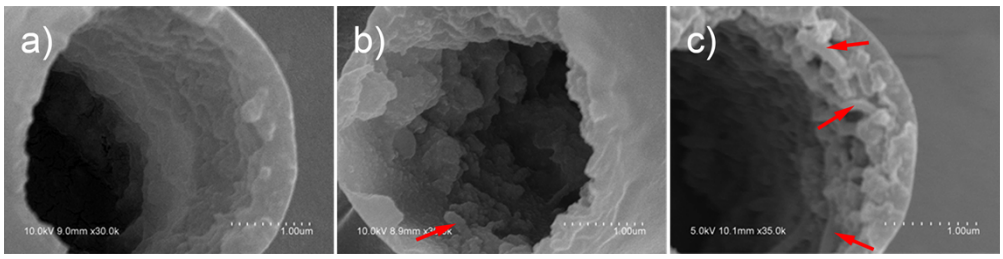

Fig. S3. SEM images of a) PEDOT/PtNP@CNT-PANI, b) PEDOT/PtNP@CNT-PEDOT, and c) PEDOT/PtNP@CNT-PPy.

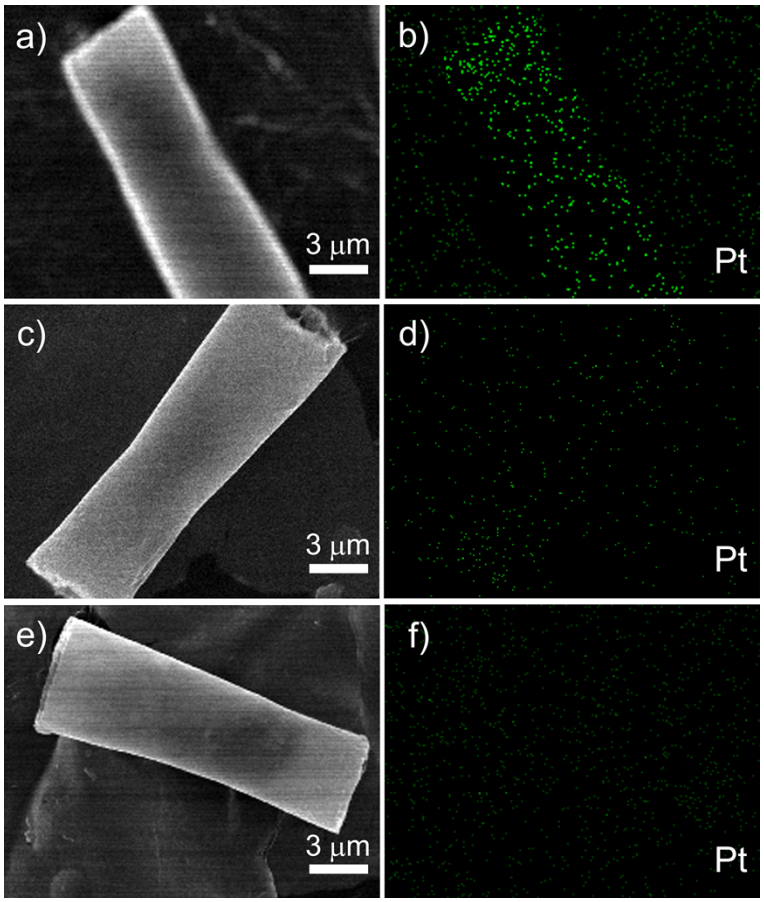

Fig. S4. EDX mapping analysis of Pt in (a,b) PEDOT/PtNP@CNT-PEDOT, (c,d) PEDOT/PtNP@CNT-PANI and (e,f) PEDOT/PtNP-PPy micromotors.

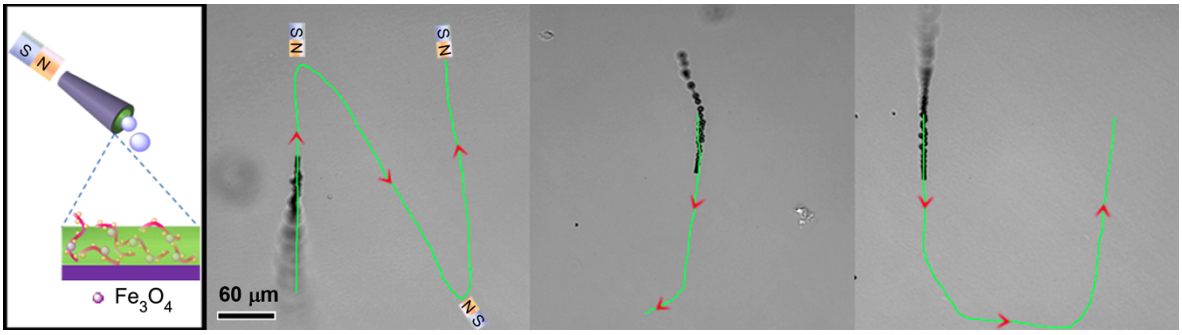

Fig. S5. Magnetically steered micromotors along predetermined N, J, U routes in a magnetic field.

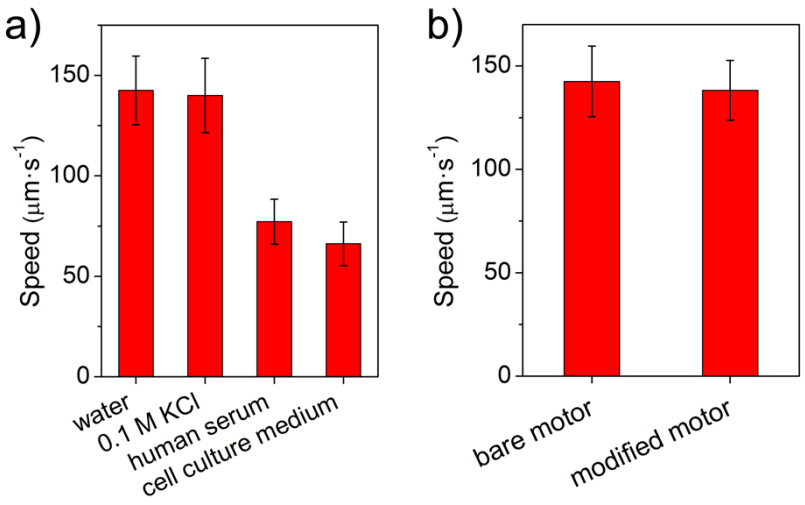

Fig. S6. Dependence of average speeds of a) PEDOT/PtNP@CNT-PPy micromotors in different media and b) bare and WGA modified micromotors in 0.01 M PBS (pH 7.4). Error bars represented the standard deviations of speeds from 20 micromotors.

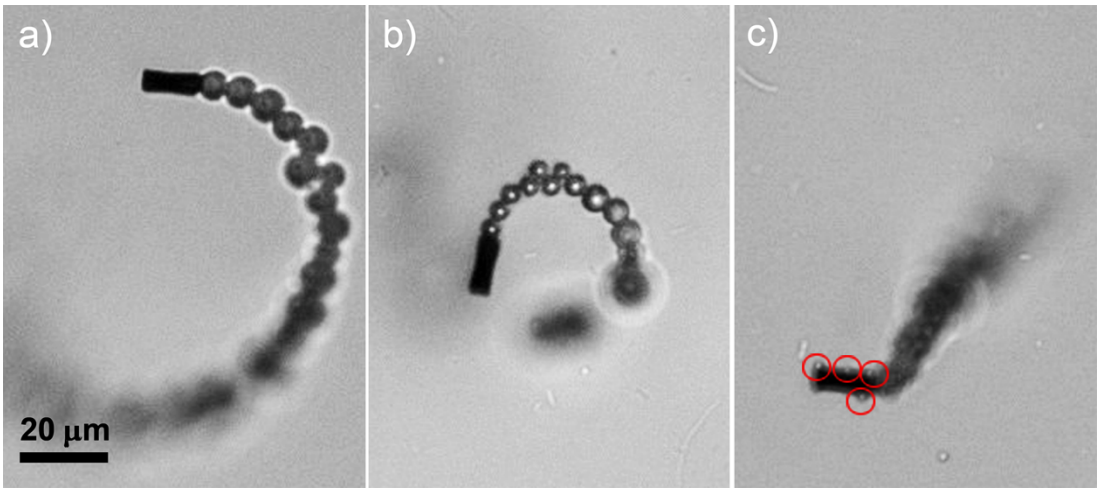

Fig. S7. Time-lapse images of a) WGA modified PEDOT/PtNP@CNT-PPy in 0.01M PBS (pH 7.4), b) bare and c) WGA modified PEDOT/PtNP@CNT-PPy in Luria-Bertani broth containing 1.8×10^5 cfu *E. coli*, in the presence of 2% H_2O_2 and 1.6% (w/v) sodium cholate, after 3 min navigation.

Table S1. Pt content ratios of the micromotors from EDX mapping analysis.

Sample	Element	Weight percentage (%)	Atomic percentage (%)
PEDOT/PtNP@CNT-PPy	Pt	25.80	2.30
PEDOT/PtNP@CNT-PEDOT	Pt	18.91	1.54
PEDOT/PtNP@CNT-PANI	Pt	8.83	0.68
PEDOT/PtNP-PPy	Pt	4.48	0.32

Supporting references

S1. R. Akter, M. A. Rahman, C. K. Rhee, *Anal. Chem.,* 2012, **84**, 6407−6415.

S2. W. Gao, S. Sattayasamitsathit, A. Uygun, A. Pei, A. Ponedal, J. Wang, *Nanoscale,* 2012, **4**, 2447−2453.

S3. Q. H. Min, X. X. Zhang, H. Y. Zhang, F. Zhou, J. J. Zhu, *Chem. Commun.* 2011, **47**, 11709–11711.

S4. A. Ambrosi, M. T. Castañeda, A. J. Killard, M. R. Smyth, S. Alegret, A. Merkoçi, *Anal. Chem.,* 2007, **79**, 5232−5240.