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Ageing Influences the Performance of Tubular Platinum Microrobots

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ABSTRACT

Autonomous self-propelled nano and microrobots are in the forefront of materials research. The micromachines are typically prepared in batches, stored and subsequently used. We show here that storage of platinum tubular catalytic microrobots in water causes their corrosion which results into the lower mobility and performance. This has important implications for construction and storage of these autonomous micromotors.

INTRODUCTION

Self-propelled nano and micromachines have garnered great interest among researchers and they are an emerging paradigm in nanotechnology.^{1,2} Nano/micromotors have attracted immense

research attributed to their ability to travel and propel over considerable distances. In recent years, there are many efforts towards the modification and functionalization of tubular micromotors for practical on-site applications especially in medicinal applications such as drug delivery,^{3,4,5,6,7} environmental remediation,^{8,9,10,11} sensing applications^{12,13,14} and microfluidic devices.^{13,15} Presently, researchers have fabricated different types and shapes of tubular self-propelled micromotors with great control on their physical characteristics.^{16,17,18,19} However, despite the progress in the applications of micromotors, there is insufficient knowledge available on their stability and durability over prolonged periods of time. It was shown previously that Cu/Pt micromotors undergo corrosion in the running H_2O_2 solution in the presence of surfactant.²⁰ Corrosion effects may pose to be a major obstacle, especially so in biological studies with harsh experimental conditions, where it reduces and inhibits the functions of the fabricated microrobots.^{21,22,23} To counter this problem, micromotors have been fabricated with modified outer surfaces to prolong their working capabilities and efficiency. Various physical properties such as lengths and diameters at different parts of the tubular micromotors, as well as surface morphology, play important roles in the nonlinear dynamics outcome of micromotors and are known to greatly affect and influence their motion.^{24,25} The influence of ageing of the micromotors in ‘storage’ conditions, the difference between performance of ‘fresh’ and ‘old’ micromotors shall have a significant impact on the reliability and reproducibility of the micromotors. Despite that, the fundamental understanding on the stability of platinum micromotors over a prolonged period of time is still unexplored and not well documented. Herein, we study the influence of ageing of micromotors on their structural stability and motion.

EXPERIMENTAL

Materials

The cyclopore polycarbonate membranes (Whatman, USA) with 5 μm pores diameter were used. SDS was purchased from Sigma-Aldrich (Czech Republic). Hydrogen peroxide of 35% was from Alfa Aesar (Singapore). Electrodeposition was carried out using by Ag/AgCl and platinum (Pt) electrodes (CH Instruments, USA). The platinum (Pt) solution was purchased from Technic Inc., USA. Deionized water with resistivity of 18.2 $\text{M}\Omega\text{ cm}$ was obtained from Milli-Q purification system (Millipore, MA, USA) and used to prepare all solutions.

Apparatus

Scanning electron microscopy (SEM) was performed using JEOL JSM 7600F (JEOL, Japan) to obtained SEM images. All pictures and videos were captured by optical microscope (Nikon Eclipse) and software (Nikon NIS-Elements). NOVA software version 1.8 connected to the Autolab PGSTAT 101 electrochemical analyser (Eco Chemie, Netherlands) was used for electrochemical deposition. The deposition was carried out in the system connected with three electrodes. Platinum (Pt) electrode was used as a counter electrode and Ag/AgCl as reference electrode. Sputtering and ultrasonication processes were performed using by JEOL JFC-1600 Auto Fine Coater and Fisherbrand FB 11203 ultrasonicator. All experiments were carried out at room temperature (25 $^{\circ}\text{C}$). Beckman Coulter Allegra 64R centrifuge was used for centrifugation process.

Preparation of tubular platinum micromotors

Cyclopore polycarbonate membrane with 5 μm pores diameter was used as a template during the electrochemical deposition process. Sputtering process was carried out with a silver target. Electrochemical deposition experiment was carried out using a three-electrode system with Ag/AgCl as reference electrode and platinum as counter electrode. The working electrode was made by connecting copper strips to the sputtered membrane. The membrane was placed into a customized electrochemical deposition cell. Platinum was galvanostatically electrodeposited at -20 mA for a duration of 2400 s. Subsequently, the membrane was washed with deionized water eight times (8 ml per wash). The washed membrane was next polished with alumina powder (5 μm) to remove the previously sputtered silver. The polished membrane was dissolved in methylene chloride. The tubular micromotors were collected by centrifugation at 8,000 rpm for 3 min and cleaned three times with methylene chloride. The cleaning process is continued with ethanol and water, three times each using the centrifuge (3 min) after each washing step. The tubular micromotors were stored in deionized water at 25 °C.

Motion control of platinum micromotors

The micromotors were moved in this experiment using the aqueous solution and changing different concentrations of hydrogen peroxide in 0.25 wt% of SDS. Hydrogen peroxide (concentration of 3% or 5%), SDS and water are mixed, and 10 μL of the mixture was dropped on a clean glass slide. The average value of velocities and standard deviation were measured for every point of the figures. 30 measurements were taken into account.

RESULTS AND DISCUSSION

We set forth to study the effect of ageing of Pt tubular micromotors on their viability and mobility. We will show that extended storage of Pt catalytic tubular motors in water solution decreases their mobility. From our previous findings, the presence of surfactant was found to promote corrosion of micromotors.²⁰ With this information in hand, surfactant (SDS) was not added into the storage solution to eliminate additional external factors which promote corrosion of micromotors.

Velocities of freshly prepared and 28 days old platinum micromotors were measured for comparison purposes. The average velocities measured will provide quantitative information to better compare the efficiency of freshly made and ‘old’ micromotors. The average velocities of micromotors were found to decrease over the duration of 28 days. The average velocity of micromotors in 3% hydrogen peroxide at day 1 was 91.1 $\mu\text{m/s}$ and it decreased to 40.1 $\mu\text{m/s}$ after 28 days of storage (day 28), as shown in Figure 1. This decrease in velocity correlates to a decrease in efficiency of the tubular micromotors by 46% over the 28 days period. The experiment was repeated with a higher hydrogen peroxide concentration to reaffirm our findings. A similar trend was observed with 5% H_2O_2 concentration over 28 days (Figure 2). The average velocity of micromotors decreased from 117.5 $\mu\text{m/s}$ (day 1) to 45.9 $\mu\text{m/s}$ (day 28). A similar decrease in efficiency of the micromotors can be inferred with a decrease in average velocity by 61%. The standard error of mean obtained is the average of 10 different days during the experimental duration where 30 different micromotors were analysed per day of analysis. The error bars obtained were thus a result of same day repeatability of measurements. When applying the one-way ANOVA statistical analysis with a confidence interval of 0.95, $p < 0.05$ was obtained

for both concentrations which suggests that the mean values of the average velocities obtained at the different days of analysis were different.

Upon comparison of both hydrogen peroxide concentrations, one noticeable trend was the higher average velocities obtained with 5% H_2O_2 . This result is in accordance with the fact that the velocities of micromotors increase with H_2O_2 concentration because of the increase rate of decomposition of H_2O_2 by platinum.^{26,27} The differences in morphologies between the two sets of tubular micromotors (day 1 and day 28) affect the efficiency and play a significant role towards the reproducibility of experimental analysis. It is worth to note that the significant decrease in average velocity of the tubular micromotors was observed 4 days post fabrication in both hydrogen peroxide concentrations. This suggests an affordable shelf-life of about 4 days post fabrication of micromotors for reproducible results with high efficient micromotors.

Figure 1. Change in average velocities of Pt tubular micromotors in 3% hydrogen peroxide over a period of 28 days. Data was collected from 30 independent measurements to obtain the average velocity. Experimental conditions: 0.25 wt% SDS at room temperature (25 °C).

Figure 2. Change in velocities of Pt tubular micromotors in 5% hydrogen peroxide over a period of 28 days. Data was collected from 30 independent measurements to obtain the average velocity. Conditions in all experiments: 0.25 wt% SDS at room temperature (25 °C).

We next investigated the morphology changes of the platinum tubular micromotors upon fabrication (day 1) and 28 days after fabrication (day 28). This will provide visual insights to the possible reasons for the decreased mobility of the micromotors. The dimensions and surface morphology of the different micromotors were analysed and compared using scanning electron microscopy (SEM). Figure 3(A) and (B) shows the SEM images of micromotors for the different time periods. Initial visual comparisons of the SEM images showed that the micromotors retained their tubular configuration over the duration of study. However, upon comparing Figures 3B(i) and B(ii), there are apparent visual differences to the surface morphologies of the two sets of micromotors. As compared to the freshly-prepared micromotors (Figures 3A(i) and 3B(i)), it was observed that the outer surface of ‘old’ micromotors (Figure 3A(ii) and 3B(ii))

appear highly corroded which would imply that the interior is corroded as well. Upon analysis of the dimensions, it was noted that the average length of micromotors decreased from (16.1 ± 1.7) μm at day 1 to (13.9 ± 0.7) μm at day 28. It was interesting to note that the diameters at the opposite ends of the tubular micromotors remained almost unchanged over the 28 days duration; (5.7 ± 1) μm and (4.3 ± 0.8) μm at day 1 vs. (5.5 ± 0.7) μm and (4.3 ± 0.6) μm at day 28. The data was acquired by measuring the three different parameters (length and diameters on opposite end) of 30 samples where the average was then obtained. Whilst shortening of the motors is small, the corrosion of their surface is significant.

From the energy dispersive X-ray spectroscopy (EDS) images obtained (Figure 3C) for that of platinum, the percentage of platinum decreases by 55.9 wt% over the period of storage. The decrease in the size of the micromotors over the time period can be attributed to the oxidation of platinum by oxygen gas dissolved in deionized water resulting in the formation of platinum salt crystals. The crystals formed could have dissolved or flaked off the micromotors thus contributing to the loss of elemental platinum. This could have accounted for the corrosion effects observed in the SEM images obtained (Figures 3A and 3B). As a result, the functionalization of platinum micromotors is performed to not only enhance motion, it also aids in reducing the rate of corrosion which in turn increases the life span of micromotors.^{28,29}

Figure 3. Scanning electron microscopy (SEM) images of (i) freshly-prepared and (ii) old platinum tubular micromotors at magnification of (A) 10 000 X and (B) 5 000 X. (C) Energy dispersive X-ray (EDX) spectroscopy maps showing distribution of platinum of (i) freshly-prepared and (ii) old platinum tubular micromotors. Scale as indicated in the respective images.

CONCLUSION

We investigated the changes in physiological and physical properties of Pt tubular micromotors which were stored in deionized water in the absence of surfactant (SDS) for different period of time. Throughout the experiment duration of 28 days, the micromotors decrease in length and the surface undergoes significant corrosion. The storage and corrosion had a significant influence on the motion of micromotors. The average velocities of the tubular micromotors dropped by 46% and 61% of the initial values in 3% and 5% hydrogen peroxide respectively. The micromotors appear to be stable for 4 days post fabrication for reproducible and efficient measurements. Henceforth, it would be of importance to prepare new sets of micromotors for enhanced efficiency and reproducibility of experimental analysis.

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