ChemPubSoc Europe

DOI: 10.1002/chem.201304804

CHEMISTRY
A European Journal
Full Paper

Sensors

Biomimetic Artificial Inorganic Enzyme-Free Self-Propelled Microfish Robot for Selective Detection of Pb^{2+} in Water

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Abstract: The availability of drinking water is of utmost importance for the world population. Anthropogenic pollutants of water, such as heavy-metal ions, are major problems in water contamination. The toxicity assays used range from cell assays to animal tests. Herein, we replace biological toxicity assays, which use higher organisms, with artificial inorganic self-propelled microtubular robots. The viability and activity of these robots are negatively influenced by heavy metals, such as Pb^{2+}, in a similar manner to that of live fish models. This allows the establishment of a lethal dose (LD_{50}) of heavy metal for artificial inorganic microfish robots. The self-propelled microfish robots show specific response to Pb^{2+} compared to other heavy metals, such as Cd^{2+}, and can be used for selective determination of Pb^{2+} in water. It is a first step towards replacing the biological toxicity assays with biomimetic inorganic autonomous robotic systems.

Introduction

Detection of water pollutants is an important but challenging task. Thus to say, to be proactive rather than being retroactive in solving problems surrounding aquatic pollution is of utmost importance.[1,2] Through early detection, appropriate preventive measures could be taken without the actual need of a remediation step. The response of living organisms towards aquatic contamination has been one of the frontlines of defense against the pollution of water bodies.[3–5] Behavioral studies and mortality rates of fish have been demonstrated to both identify and quantify the amount of contaminants in water.[3,4] However, given the absence of clear guidelines, consistency and the sheer human capital and technological intensiveness required of such a set-up, the implementation is extremely difficult.[6] Hence, this arises a need for a robust, simple, and scalable system that can be easily implemented and has ease of operation.

Micromotors are new self-propelled materials at the forefront of materials science that can move autonomously to perform specific tasks.[7–12] These micromachines or microrobots hold great promise in numerous fields. They have been demonstrated to be able to carry out a wide spectrum of work including those in biomedical applications,[13] cargo delivery,[14] and environmental remediation.[15,16] Amongst all, the bubble-ejection propulsion mechanism in a tubular catalytic engine, which utilizes hydrogen peroxide as its fuel, is one of the most intensively studied model.[12,17] These microjets have been shown to be able to navigate through real-world environments: from the water bodies of lake water and sea water to tap water.[18] However, the surrounding chemical environment has also been demonstrated to have pronounced influence on the very behaviors of these microjets.[19,20] Recently, Orozco et al. developed enzyme-powered bubble-propelled micromotor, dubbed "microfish" for sensing pollutants, such as Hg^{2+}, Cu^{2+}, or aminotriazole.[21] It was argued that such artificial enzyme-powered microfish can play the same role as live fish, obviating the need to use living organisms for toxicity assays. The downside of such artificial enzyme-powered microfish is that it is not selective to different pollutants and also that the enzyme layer (which is the sensitive layer) has limited shelf-time due to its biological nature. Herein, we obviate the use of enzyme and show that artificial inorganic (enzyme-free) microfish can be used for selective sensing of Pb^{2+} in water.

The increase of heavy-metals concentration in the environment has been associated with anthropogenic activities, especially that of the burning of fossil fuels and industrial activities.[22] This is of particular concern, because the accumulation of such pollutants is detrimental to human health.[23] Platinum has been demonstrated to show sensitivity towards poisoning effects, because minute concentrations of heavy metals are known to retard the efficiency of catalytic convertors[24,25] and also inhibit organic reactions during catalysis.[26] To evaluate the effects of poisoning by heavy metals, the decomposition of hydrogen peroxide over platinum has been used as a model of study.[27] Herein, we explored the possibility of using bubble-propelled Pt microfish robots to establish a correlation between their activity and the presence of heavy-metal ions of Pb and Cd. A decrease in microjet activity can be attributed to the poisoning of the Pt microfish robot and the change in chemical environment. In the following sections, the use of

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304804.

a simple optical visualization of the microfish robots, allows for a facile inference to the type of pollutants that is present.

Results and Discussion

Herein, we demonstrate that inorganic enzyme-free Pt-based microfish robots can selectively sense presence of Pb^{2+} in water. The microfish robots are powered by the bubble propulsion caused by the catalytic decomposition of hydrogen peroxide at its inner surface of platinum to oxygen. The expulsion of the bubble at the ends propels the microfish robots forward. The influence of heavy metals over the viability of microfish robots was investigated. Two principal representative ions of Pb^{2+} and Cd^{2+}, commonly present in polluted water, were used as poisons to cripple the inorganic Pt microfish robots.[23] Ultrapure water was used as the control environment to which the motion of the microfish robots can be compared. Two observable physical attributes obtained from the microfish robots were used to evaluate the propulsion of the microfish robots: the number of microfish robots, which are expelling bubbles and the number of microfish robots exhibiting motion due to the bubble propulsion. The average velocities and the corresponding standard deviation were taken. Selective introduction of the heavy metals of Pb^{2+} and Cd^{2+} were carried out at appropriate concentrations to poison the inorganic Pt microfish robots.

The motion of the microfish robots was first evaluated in ultrapure water. As illustrated in Figure 1, 100% of the microfish robots that ejected bubbles demonstrated mobility in ultrapure water. Then, selective introduction of the heavy-metal salt of $Pb(NO_3)_2$ was carried out. At 0.48 mM concentration of $Pb(NO_3)_2$ (100 ppm of lead), only 72% of the microfish robots were bubbling, and 67% of them demonstrated bubble-propulsion motion. The gradual decrease in bubble ejection and microjet propulsion was recorded across increasing concentrations of $Pb(NO_3)_2$, until a concentration of 1.92 mM at which bubble ejection at 24% and bubble-propelled motion at 21% were recorded. To make sure that the Pt microfish robot is specifically reacting to Pb^{2+} and not to any inorganic compounds, we looked into the literature. When the ionic strength of the KNO_3 was compared to 1.92 mM of $Pb(NO_3)_2$ at appropriate levels, there was little disabling of the microfish robots with approximately 75% of them remaining active for bubbling and microjet propulsion.[18] This was indicative that in addition to the changes in ionic strength due to the introduction of $Pb(NO_3)_2$, an additional mechanism of poisoning and disabling of the microfish robots was present, namely, the poisoning of Pt surface by Pb^{2+}.

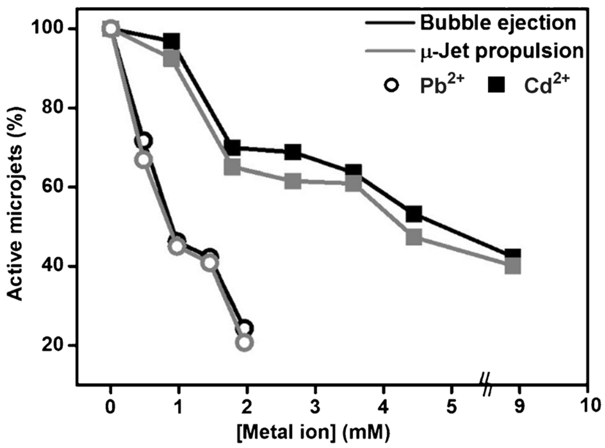

Figure 1. Percentage of active microfish robots showing bubble ejection (black line) and moving by microjet propulsion (grey line). Poisoned with selected concentrations of $Pb(NO_3)_2$ (○). Poisoned with selected concentrations of $Cd(NO_3)_2$ (■). Ultrapure water was used in the control experiment, in which both the running and bubbling percentages were defined as 100%. Conditions in all experiments: 23 °C, 3 wt% of H_2O_2, and 1 wt% SDS.

In Figure 1, the correlation between bubble ejection and mobility with the introduction of a Cd^{2+} poison through $Cd(NO_3)_2$ was investigated. At 0.89 mM of $Cd(NO_3)_2$ (100 ppm of cadmium), 97% of the microfish robots were bubbling, and 92% of them were exhibiting propulsion. This was in contrast to the large decrease in bubbling and propelled microfish robots in $Pb(NO_3)_2$ at the similar molar concentrations at which only 46% of the microfish robots were bubbling, and 45% of them were exhibiting propulsion. The behavior of microfish robots under influence of 1.78 mM $Cd(NO_3)_2$ demonstrated similar behavior to that of under influence of KNO_3 at comparable concentrations at which about 75% of the microfish robots were demonstrating both bubble ejection and propulsion motion. A slowly tapering decrease in both bubble ejection and propulsion amongst the microfish robots was observed with increasing concentrations of $Cd(NO_3)_2$ and KNO_3. This recurring similar trend between the two salts demonstrates that the increment in ionic strength adversely affected the motion of microfish robots as was observed by Zhao et al. in their work on chemical environments[18] and Wang et al. with blood electrolytes.[20] Only at a concentration of 8.9 mM of $Cd(NO_3)_2$ was observed that more than 50% disablement of the microfish robots (LD_{50}: the concentration of a given agent, which is lethal to 50% of the artificial microfish robots) in bubble ejection and microjet propulsion could be achieved.[21]

For the ease of comparison, the concentration of heavy-metal ions, which was able to poison the number of microfish robots bubbling and demonstrating mobility to less than 50% (LD_{50}), was used as a gauge. In the case of $Pb(NO_3)_2$, the amount of 0.96 mM of Pb^{2+} was required. On the other hand, 8.9 mM of $Cd(NO_3)_2$ was required to reduce the number of microfish robots exhibiting bubbling and microjet propulsion below 50% (LD_{50}). This is a clear indication that platinum-based microfish robots are highly sensitive to the presence of lead ions compared to cadmium, and that they are able to detect the presence of lead down to micromolar concentrations, as was demonstrated by the drastic drop in active microfish robots in the presence of 0.48 mM of Pb^{2+}. This is in the same order of magnitude as the heavy metals found in effluents from industrial plants[28–29] and sludge materials.[30] Notably, at these concentrations, heavy metals disrupt the ability of cellular ion channels to perform modulation, causing serious health concerns.[31–32]

Figure 2 illustrates the velocity of the microfish robots with increasing concentrations of heavy metal ions. During the con-

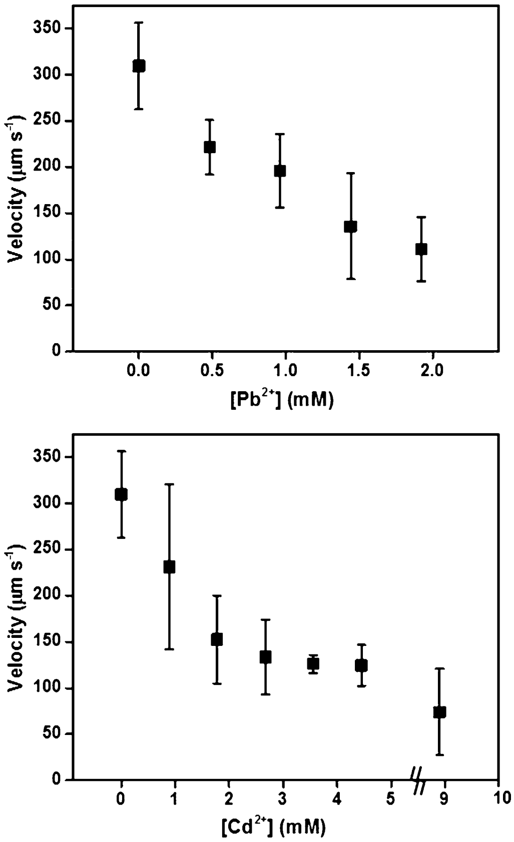

Figure 2. Velocity of Pt-catalyzed microfish robots in electrolyte solution. a) Poisoned with selected concentrations of $Pb(NO_3)_2$. b) Poisoned with selected concentrations of $Cd(NO_3)_2$. Conditions in all experiments: 23 °C, 3 wt% of H_2O_2, and 1 wt% SDS.

trol experiment in the absence of heavy metals, the microfish robots demonstrated an average velocity of 310 $\mu m\,s^{-1}$. This is in line with previous velocities reported by our group, with the microfish robots fabricated by an electrochemical template procedure, achieving an average velocity of 365 $\mu m\,s^{-1}$.[18–20] With the introduction of 0.96 mM of $Pb(NO_3)_2$ shown in Figure 2a, the velocity of the microfish robots dropped to 196 $\mu m\,s^{-1}$. This is in contrast to the case of $Cd(NO_3)_2$ at 0.89 mM shown in Figure 2b, in which the velocity of the microfish robots remained considerably higher compared to the $Pb(NO_3)_2$ at 231 $\mu m\,s^{-1}$. The Pb^{2+} poisoned microfish expressed a steady decrease in velocity to about 110 $\mu m\,s^{-1}$ at a concentration of 1.92 mM compared to Cd^{2+} poisoned microfish robots, in which a relatively steady velocity between approximately 125 to 150 $\mu m\,s^{-1}$ was reached at concentrations above approximately 1 mM. It was only observed at 8.9 mM of $Cd(NO_3)_2$ that the velocity of microfish dropped to 74 $\mu m\,s^{-1}$. The phenomena observed with $Cd(NO_3)_2$ was analogous to the phenomena observed with KNO_3, in which during concentration increase, the velocities of the microfish robots was held relatively constant at approximately 150 $\mu m\,s^{-1}$.[18] The similarities of the observations under influence of $Cd(NO_3)_2$ and KNO_3 for microfish robots demonstrate that the reduction in activity was mostly due to changes in ionic strength. However, in the presence of Pb^{2+}, an additional poisoning mechanism of the microfish took place.

The differing behaviors of the heavy-metals-poisoned microfish robots could be explained as follows. Pb^{2+} is known to be strongly adsorbed on the platinum: these ions cover the active sites of the platinum, resulting in the decrease in activity of the platinum catalytic sites.[25] Many reports have shown that the adsorption of the lead ion on platinum is irreversible,[33] and it is often termed as a permanent poison.[34] But in contrast, adsorption of Cd^{2+} was noted to be weaker, and the interactions are likely to be reversible.[35–37] The decreased bubbling at Pb^{2+}-poisoned microfish was coupled with decreased activity and velocity. Evidently, the main mechanism of bubble propulsion has been retarded, resulting in the loss of motility.

This could be explained by electronegativity of the Pb^{2+} ions. Lead, with an electronegativity of the 2.33 on the Pauling scale, is considerably more electronegative than the value of 1.69 for cadmium.[38] The adsorbed atoms of Pb are likely to be strongly attached on the surface of platinum during adsorption compared with Cd, resulting in the greater degree of poisoning, as demonstrated herein. The atomic size of lead is also larger than cadmium, covering more active sites on the platinum surface, effectively disabling the microfish robots further. In another independent study of a self-electrophoretic Pt/Au nanorod, a similar but less accentuated trend was also observed between the presence of Pb^{2+} and Cd^{2+}, illustrating the poisoning effects of Pb^{2+}.[39]

However, organosulfur compounds also inhibit the activity of microfish to similar degrees[19] and the presence of red blood cells retard their movement.[40] Therefore, the contextual space, in which the microfish are applied, must be considered. More work is still required for the use of this proof-of-concept device for selective detection of compounds against a general setting.

The differing behavior of the microfish robots towards heavy-metal ions of Pb^{2+} and Cd^{2+} allowed a selective inference of the type of ions that are present in the solution. Although colorimetric methods,[41] self-electrophoretic nanomotors,[39] and enzyme-powered microfish[21] face selectivity limitations for heavy metals at high micromolar concentrations, these Pt-based microfish demonstrated aptitude at these ranges. This opens a simple pathway towards identifying the type of inorganic substances present in aquatic sources. The study of the activity and mobility of the inorganic Pt microfish robots allows a facile detection of the lead ions over cadmium.

Conclusion

The effects of poisoning of inorganic Pt microfish robots were systematically studied with the selective introduction of the heavy-metal salts $Pb(NO_3)_2$ and $Cd(NO_3)_2$. A greater decrease in the activity and the velocity of inorganic Pt microfish robots were observed during poisoning with $Pb(NO_3)_2$ compared to $Cd(NO_3)_2$. The inherent properties of the lead ion-adsorption behavior with platinum resulted in the decreased activity of the inorganic Pt microfish robots compared to Cd^{2+}. The differentiating behavior of Pb^{2+} with inorganic Pt microfish robots allowed the selective detection of Pb^{2+} over Cd^{2+}. This allowed a potential pathway for a continuous monitoring of pollutants by an optical visualization of the activity and mobility of the inorganic Pt microfish robots.

Experimental Section

Materials

The cyclopore polycarbonate membranes with pores of 2 μm in diameter were purchased from Whatman, USA (cat. no. 7060–2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella, Inc., USA. Hydrogen peroxide (35%) was purchased from Alfa Aesar, Singapore. Methylene chloride and ethanol were purchased from Tedia, USA. Pt electrodes with 1 mm diameter and Ag/AgCl/1 м KCl were purchased from CH instruments, USA. The platinum-plating solution was obtained from Technic Inc., USA. $CuSO_4\cdot 5H_2O$ (98+%), sodium dodecyl sulfate (SDS), $Pb(NO_3)_2$, and $Cd(NO_3)_2\cdot 4H_2O$ were purchased from Sigma–Aldrich. Chemicals were used as received, and the solutions were prepared by using ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system.

Apparatus

Electrochemical deposition was carried out with a μAutolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (23 °C) by using a three-electrode arrangement. A platinum electrode was utilized as a counter-electrode, and Ag/AgCl was used as the reference electrode. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software.

Preparation of Cu/Pt concentric bimetallic microtubes[42]

The Cu/Pt concentric bimetallic microtubes were synthesized with a modified electrochemical deposition procedure on a cyclopore polycarbonate template, and they were referred as "microfish robots" in the following discussion. Colloidal graphite ink was applied on the one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminium foil was attached to the ink immediately, which serves as the working electrode for the plating experiments. The template was assembled into a customized electrochemical deposition cell. Platinum counter electrode and Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out with a μAutolab type III electrochemical analyzer connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software. The template was rinsed with ultrapure water (5 mL; 18.2 MΩ cm) for four times, and the Cu outer layer was deposited galvanostatically at −4 mA for 450 s. The deposition solution contained 1 м $CuSO_4$. Consequently, after removing the deposition solution, the template was rinsed five times with water (8 mL). The platinum segment was electrodeposited subsequently at −4 mA for 450 s, by using the commercial plating solutions. When the deposition of microtubes was finished, the electrochemical cell was disassembled, and the template was washed five times with water (8 mL). After that, the template was ultrasonicated for three times in ultra-pure water (2 mL) for 3 min each time. The graphite layer was removed during the ultrasonication procedure. The template was placed in an Eppendorf tube with methylene chloride (2 mL) and ultrasonicated, until the whole template was dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly three times with methylene chloride. The solution was then washed with ethanol and water two times each and centrifuged for 3 min after each washing step. The tubes were stored in water at room temperature.

Operation of microfish robots

The experiments for studying the influence of heavy metals on the motion of microfish robots were carried out in an aqueous solution containing hydrogen peroxide (3 wt%) at constant surfactant concentrations (1 wt% of SDS). A mixture of microfish robots (7 μL), SDS (1 wt%), H_2O_2 (3 wt%), and appropriate concentrations of the heavy-metal salts of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ were applied on a glass slide that was freshly cleaned with nitrogen gas. Statistics from the number of microfish within a reading is given in the Supporting Information.

Acknowledgements

J.G.S.M. is supported by the National Research Foundation Singapore under its National Research Foundation (NRF) Environmental and Water Technologies (EWT) PhD Scholarship Programme and administered by the Environment and Water Industry Programme Office (EWI).

Keywords: aquatic pollution · heavy metals · micromotors · platinum · sensors

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Received: December 7, 2013
Revised: February 17, 2014
Published online on March 20, 2014

