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Epitaxial-assembled monolayer superlattices for efficient micromotor propulsion

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Abstract

Exploring micromotors with outstanding propulsion efficiency is of great importance for aspects ranging from enhancement of performance to realization of applications. Improvements in propulsion efficiency lead to a lower fuel requirementand broadens the potential application areas for higher environment compatibility. In this article, a tubular micromotor with catalytic nanoparticle superlattices is fabricated through a simple epitaxial assembly method. A high surface-to-volume ratio due to the use of catalytic nanoparticles, a carbon outer layer and cooperative propulsion of multitubes enables the micromotor to move in biocompatible environment with a low concentration of fuel. In addition, magnetic nanoparticles are integrated into the micromotor to offer effective control of the direction of movement by using a magnetic field. This work provides a simple and low-cost fabrication method for a micromotor with high performance, which is expected to meet practical demands.

Supplementary material for this article is available online

Keywords: nanoparticle superlattices, micromotor, tubular microstructure, self-assembly

(Some figures may appear in colour only in the online journal)

1. Introduction

With the development of nanotechnology, micro/nanomotors attract great attention for their capabilities in diverse applications such as cargo delivery [1–3], molecular detection [4–6] and environmental decontamination [7–9]. Among various mechanisms and geometries, bubble-propelled tubular micromotor opens up a tantalizing prospect due to their impressive features, including considerable freedom with a functionalized layer, concentrated generation of thrust [10] and negligible toxicity effects [11]. Rolled-up nanotechnology [12] and template electrodeposition [13] are employed to fabricate

tubular micromotors with catalytic modification on inner surfaces. Unfortunately, rolled-up tubular micromotors require complex top-down photolithographic processes and expensive clean rooms. In addition, the wet-etching process for removing the sacrificial layer may destroy the hollow structure due to surface tension [14]. On the other hand, galvanostatic deposition of the catalytic layer in template electrodeposition suffers from non-uniform coating thickness, which destroys structural uniformity [15]. Therefore, there is an emergent requirement to develop a simple fabrication method for highperformance micromotors with the high utilization of expensive catalysts.

Self-assembly of long-range-ordered nanoparticle arrays, known as nanoparticle superlattices [16], is an efficient and

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low-cost technique to construct complex three-dimensional structures with arbitrary functional materials [17], thus making them ideal for designing metamaterials and nanodevices [18]. Nanoparticles offer particular properties different from those of their bulk equivalents, especially high catalytic efficiency thanks to their large surface-to-volume ratio and a good deal of available active sites per unit area [19]; so, numerous studies have reported nanoparticles supported on both solid surfaces and colloidal ones [20]. In this work, a carbon tubular micromotor with catalytic superlattices is proposed through epitaxial assembly of monolayer Pt nanoparticles inside a porous anodized aluminium dioxide (AAO) template. The tubular structure is stabilized by in situ ligand carbonization, and the micromotor is released by selective etching of AAO. High surface-to-volume ratio provided by monolayer Pt nanoparticle superlattices leads to sufficient utilization of the surrounding fuel. Benefiting from the cooperative behavior of a bunch of micromotors, prominent motion speed and moving ability in a low fuel concentration are obtained. Furthermore, the versatility of this epitaxial-assembly method allows us to incorporate Fe₃O₄ nanoparticles into the system, endowing the micromotor with directional tunability via magnetic field. Our work offers a convenient and low-cost fabrication method for high-performance tubular micromotors, with the capability of further modification for promising applications.

2. Methods

2.1. Materials

Platinum(II) 2,4-pentanedionate (Pt(acac)₂; Pt 48% min) was obtained from Alfa Aesar. Oleylamine (OAm; 70%), oleic acid (OA; 90%), sodium oleate (99%), 1-octadecene (ODE; 90%) and benzyl ether (98%) were purchased from Aldrich. Iron chloride hexahydrate (FeCl₃·6H₂O) and sodium dodecylbenzenesulfonate (SDBS; C₁₈H₂₉NaO₃S) were purchased from Aladdin. Manganese carbonyl (Mn₂(CO)₁₀; 98%) was purchased from J&K Chemical. AAO membranes with pore width of ~400 nm and length of ~60 μ m were purchased from Shanghai Shangmu Technology Co. Ltd. Hydrogen peroxide (H₂O₂; 30%), chloroform (CHCl₃), hexane, ethanol and methanol were purchased by Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification. Iron oleate was prepared by reacting sodium oleate with FeCl₃·6H₂O.

2.2. Synthesis of Pt and Fe₃O₄ nanoparticles

Synthesis of Pt nanoparticles starts with dissolving Pt(acac)₂ (0.08 g), oleylamine (7.4 ml) and OA (1.25 ml) in benzyl ether (10 ml) at room temperature. The mixture was degassed on a Schlenk line under vacuum. Subsequently, the precursor mixture was placed in an oil bath with preheated temperature of 160 °C for 10 min. Then a mixture of $Mn_2(CO)_{10}$ (40 mg) in CHCl₃ (1 ml) was injected into the precursor mixture at 160 °C and the reaction was heated to 200 °C. After 30 min of reaction, the solution is cooled down and Pt nanoparticles were isolated by adding ethanol and centrifugation. Pt nanoparticles



Figure 1. Fabrication scheme of monolayer Pt nanoparticle superlattice tubular micromotors: (I) epitaxial assembly of Pt nanoparticles in channels of AAO template during solvent evaporation; (II) ligand carbonization for the construction of carbon microtubes with Pt nanoparticles; (III) selective etching of AAO template to release Pt nanoparticle superlattice tubular micromotors; (IV) propulsion of micromotor cluster through O₂ bubble ejection in H_2O_2 fuel.

stabilized with OA were redispersed in hexane for the next assembly stage.

As for the preparation of Fe_3O_4 nanoparticles, iron oleate (18 g) and OA (4.3 g) were dissolved in ODE (90 g) at room temperature. The mixture was degassed at 120 °C on a Schelenk line under vacuum and heated to 320 °C under N₂. The reaction was quenched after 1 h by removing the heating mantle. Fe_3O_4 nanoparticles were isolated and purified from the growth solution using methanol and ethanol followed by centrifugation. Precipitated Fe_3O_4 nanoparticles were redispersed in hexane for the next assembly stage.

2.3. Fabrication of nanoparticle superlattice tubular micromotors

The fabrication process of monolayer Pt nanoparticle superlattice tubular micromotors is illustrated in figure 1. The AAO template was immersed in hexane solution containing OA (0.2 M) for 12 h. Then, the template was moved into hexane solution with stabilized Pt nanoparticles. Then they were treated at 80 °C for solvent evaporation. During the evaporation process, efficient anchorage of monolayer Pt nanoparticles was obtained due to the match between the alkyl chain of tethered OA molecules and that of OA ligands initially adhering to the nanoparticle surface [21] (process I and II in figure 1).

Then, the AAO template containing the as-assembled Pt nanoparticle monolayer was treated by ligand carbonization. The calcination occurred at 500 °C for 2 h in N₂ atmosphere, through which OA capping ligands was transformed into a thin carbon shell covered by Pt nanoparticles. Simultaneously, OA molecules attached to AAO surface were carbonized to shape a tubular carbon wall, serving as a robust micromotor framework and facilitating biocompatibility of the micromotors. After that, the sample was simply soaked in 6 M KOH

for 1 h for selective etching of AAO template. Pt nanoparticle superlattice tubular micromotors were obtained after drying in the oven. Micromotors were separated and dispersed with ultrasonication in ethanol. These micromotors were autonomously propelled in the presence of H_2O_2 fuel through producing and ejecting oxygen bubbles. In order to achieve magnetic guidance of the micromotors, Fe_3O_4/Pt nanoparticle superlattice tubular micromotors were fabricated through the same process with the component ratio of 1:1.

2.4. Characterization

The structure of the fabricated micromotor was observed by optical microscope (BX51TRF, Olympus) and scanning electron microscopy (SEM; Ultra-55, Zeiss). Transmission electron microscopy (TEM; Hitachi) was used to characterize the morphology of nanoparticle superlattices in the tubular micromotors. Energy-dispersive x-ray spectroscopy (EDX; IXRF-550i, IXRF) was used to analyse the elemental distribution of the nanoparticle superlattice tubular micromotors.

2.5. Investigation of micromotor motility

The motion of the micromotor was recorded by optical microscope coupled with a charge-coupled device camera and analysed through ImageJ software. The motion of a bunch of micromotors was observed in 3% H₂O₂ solution containing 0.1 wt% surfactant (SDBS). Moving speed related to the concentration of H₂O₂ was investigated in the solution with 0.1 wt% surfactant. The locomotive behaviour of Fe₃O₄/Pt nanoparticle superlattice tubular micromotors was studied in 1% H₂O₂ solution with 0.1 wt% surfactant. A permanent magnet was positioned underneath a suspension of the micromotor at a distance close enough to synchronize the magnetic field with the movement of the micromotors.

In order to check the modality of the micromotor movement, the mean squared displacement (MSD) is calculated according to [22]:

$$MSD = [r(t + \Delta t) - r(t)]_t^2$$

where Δt is the time step between video frames and r is the (x,y) coordinate values from individual video tracking. Average speed of micromotor is calculated through measuring the total moving distance of the micromotor over a certain period of time.

3. Results and discussion

The tubular micromotors after selective etching of AAO template and drying are shown in figure S1 (available in the online supporting information at stacks.iop.org/JPhysD/53/274004/ mmedia), which are irregularly dispersed under optical microscope due to the collection effect during the drying process. It is proved that this epitaxial assembly is a convenient method for mass fabrication of micromotors. After ultrasonication treatment in 50% ethanol for several seconds, micromotors were separated into smaller clusters with a diameter



Figure 2. Structure of Pt nanoparticle superlattice tubular micromotors. (a) SEM image and (b) focused SEM image of tubular micromotors cluster. (c) SEM image of single tubular micromotor. (d) TEM image of single tubular micromotor. (e) TEM image of Pt nanoparticle superlattices on the inner wall of micromotor.

of ~10 μ m and a length of ~36 μ m, as shown in figure 2(a). The high-magnification SEM image in figure 2(b) presents that the microtubes are orderly arranged as the porous structure of initial AAO template, indicating successful fabrication of controllable and uniform geometry of the structure at micro/nanoscale in high yield. After treatment by ultrasonication for longer time, the cluster was separated into a single tubular micromotor as presented in figure 2(c). The length is measured as about 6 μ m, while the outer diameter is about 400 nm, which is consistent with the pore size of the AAO template. As is displayed in figure S2, the structure is tubular not solid, enabling it to eject oxygen bubbles through the hollow chamber.

The existence of Pt nanoparticle superlattices was checked through TEM. Figure 2(d) shows the image of a single Pt nanoparticle superlattice tubular micromotor. The wall, carbonized from OA capping ligands, is observed to immobilize the hollow tubular structure. The dots on the surface of tubular micromotor are considered as Pt nanoparticles. To further clarify the distribution of nanoparticles, focused TEM imaging was carried out and the result shown in figure 2(e). Unlike common micromotors where Pt is deposited with a smooth surface [12], it is noticed in our micromotor that the Pt nanoparticles with average size of 7 nm are hexagonally ordered in a monolayer. Therefore, this rough surface is expected to provide dramatically increased catalytic surface and improved propulsion efficiency.

Next, as it is proved that cooperative propulsion of multitubes would generate higher thrust power [23], the locomotive behaviour of a Pt nanoparticle superlattice tubular micromotor cluster rather than that of a single one was investigated. Figure 3(a) illustrates the time-lapse images of the tubular micromotor cluster positioned in 3% H₂O₂ solution with 0.1 wt% surfactant (video S1, supporting information). Surfactant is the prerequisite in continuous motion of bubble-propelled micromotors, which facilitates interfacial free-energy decrease and bubble detachment. The cluster



Figure 3. (a) Time-lapse motion images, (b) tracking trajectory and experimental MSD curve (inset), and (c) corresponding speed variation of a cluster of tubular micromotors in 3% H₂O₂ and 0.1 wt% surfactant. Red dashed line in (c) indicates the average speed.



Figure 4. Speed and bubble ejection frequency of the tubular micromotor cluster in the presence of H_2O_2 fuel with different concentration and 0.1 wt% surfactant.

is approximately 32 μ m long and 20 μ m in diameter. This autonomous motion results from oxygen bubbles generated through the catalytic decomposition of H₂O₂ around Pt nanoparticles. As the bubble is ejected from the end of the tube, the micromotor is propelled in the opposite direction with a change in momentum. Considering that catalyst is not consumed during reaction, new bubbles will be produced and released continuously with the existence of H₂O₂, which leads to continuous propulsion of the micromotor [24].

In order to statistically analyse movement of the micromotor cluster, the tracking trajectories, relevant MSD and speed values are further calculated. As is displayed in figure 3(b), the micromotor cluster moved in a circular path over a period of 1 s. The trace line is colour coded to depict the time progression while tracking. The inset of figure 3(b) shows that MSD values as a function of time saturate and then decrease at 0.68 s, indicating it is getting close to its starting point, which further demonstrates the round trajectories. This nonlinear path of the micromotor cluster is due to the asymmetric distribution of microtubes. An asymmetric ejection of bubbles leads to inhomogeneous fluid flow through and around the micromotor cluster, thus making the force perpendicular to the tube axis unbalanced and rotating the cluster during selfpropulsion [25]. In figure 3(c), the speed variation as a function of time is plotted with an interval time of 0.04 s, illustrating the



Figure 5. Structure of Fe_3O_4/Pt nanoparticle superlattice tubular micromotors. (a) SEM image of tubular micromotors. (b) EDX elemental characterization of carbon, iron, platinum and oxygen in tubular micromotors. (c) TEM image of the single tubular micromotor. (d) TEM image of Fe_3O_4/Pt nanoparticle superlattices on the inner wall of the micromotor.

fluctuation with a maximum of ~509 μ m s⁻¹ and a minimum of 92 μ m s⁻¹. The average speed of the micromotor cluster is ~292 μ m s⁻¹ with the standard deviation (SD) of 114 μ m s⁻¹, equivalent to eight body lengths per second.

The influence of H₂O₂ fuel concentration on catalytic motion of tubular micromotors is further demonstrated. Figure 4 shows average micromotor cluster speed and bubble ejection frequency as a function of H₂O₂ concentration (including 0.3%, 1.0%, 2.0% and 3.0%) with 0.1 wt% surfactant. Bubble frequency rapidly changes from 5 Hz to 43 Hz upon raising the H_2O_2 level from 0.3% to 3.0%. The soar over entire range of H₂O₂ concentration originates from the enhancement of chemical reaction rate. Correspondingly, the average speed of the micromotor cluster is ~34 μ m s⁻¹ in 0.3% H₂O₂ aqueous solution, which could be attained at ~297 μ m s⁻¹ in 3.0% H₂O₂ aqueous solution. Higher bubble generation frequency leads to a boosted speed of ~874% in the selected fuel concentration range. Hence, as the concentration of H_2O_2 increases, the micromotors swim more quickly. Particularly, the microtube cluster is able to show motion behaviour at



Figure 6. (a) Time-lapse images, (b) tracking trajectories and MSD curve (inset), and (c) speed variation of magnetically controlled movement of the $Pt-Fe_3O_4$ nanoparticle superlattices tubular micromotors (Motor 1) in 1% H_2O_2 and 0.1 wt% surfactant. Red dashed line in (c) indicates the average speed.

 H_2O_2 concentration as low as 0.3% (compared with 1% for smooth micromotors [26]). Due to toxicity of highly concentrated H_2O_2 to biomaterials and cells [27], Pt nanoparticle superlattice tubular micromotors are highly promising for biomedical tasks. The average speed and bubble frequency of the micromotor cluster also exhibit a positive correlation with H_2O_2 concentration under a lower concentration of surfactant (figure S3), excluding the contribution of surfactant on the excellent catalytic performance.

This excellent catalytic performance can be explained by the hugely enhanced surface area of the catalyst. Previous reports indicate that rate of oxygen generation is linearly proportional to the area of Pt surface and to H_2O_2 concentration [28–30]. For the micromotor with a smooth Pt inner surface, the oxygen productivity in H_2O_2 concentration $C_{H_2O_2}$ can be expressed as

$$\frac{\mathrm{d}V_{O_2}}{\mathrm{d}t} = nC_{\mathrm{H_2O_2}} 2\pi R_j L$$

where *n* is a rate constant experimentally estimated to be $9.8 \times 10^{-4} \text{ ms}^{-1}$, R_j and *L* is the radius and length of the tubular cavity, respectively. For superlattice tubular micromotors with a high surface-to-volume ratio of Pt nanoparticles, the inner surface area is much larger than $2\pi R_j L$, so productivity of oxygen is prominently higher than that of micromotors with smooth Pt inner surfaces, leading to the capability of obvious motion in ultra-low concentrations of H₂O. The contribution of the large surface-to-volume ratio of Pt nanoparticle superlattices is further demonstrated through comparisons with theoretically predicted speeds of micromotor with a smooth Pt surface (supplementary note 1 and figure S4)

As the accessibility of specialized and sophisticated tasks would be limited by the uncontrollable autonomous motion of micromotors, movement control can be achieved through the addition of magnetic particles [31]. So Fe₃O₄ nanoparticles were integrated into the inner walls of the Pt nanoparticle superlattice micromotors through the same fabrication process illustrated above. SEM image in figure 5(a) illustrates the tubular morphology of clustered Fe₃O₄/Pt micromotors, along with reproducibility of the method. The high-magnification image (figure S5) clearly illustrates that the resultant tubular micromotors have an average diameter of 400 nm, conforming to the pore size of the AAO template. Obvious dots dispersed on the surface are considered as Fe₃O₄ and Pt nanoparticles. EDX analysis of figure 5(b) shows the clear presence of carbon, iron, platinum and oxygen, confirming the successful combination of Fe₃O₄ and Pt nanoparticles into tubular micromotors. In addition, distribution of these elements is in accordance with the tubular geometry in the SEM image of figure 5(a).

Further characterization of a single Fe₃O₄/Pt nanoparticle superlattice tubular micromotor was carried out by TEM as illustrated in figure 5(c) and (d). Unlike hexagonally ordered spherical Pt nanoparticles, Fe₃O₄ and Pt nanoparticles are distributed stochastically without uniform size and shape. Two kinds of diameter of the nanoparticles are found. The smaller and identical ones refer to Pt nanoparticles with a diameter of 7 nm. While the larger ones are Fe₃O₄ nanoparticles, which are not constant in size with a diameter of up to 26 nm. The size is smaller than a single domain of Fe₃O₄, so Fe₃O₄ nanoparticles are expected to be superparamagnetic [32]. The random distribution of Fe₃O₄ and Pt nanoparticles is due to their strong magnetic dipole–dipole interaction, through which nanoparticles are attracted and form clusters with bigger particle size [33].

Figures 6(a) and (b) display the time-dependent images and tracking trails of the motion of two tubular micromotor clusters under magnetic guidance in the solution containing 1% H₂O₂ and 0.1 wt% surfactant (video S2, supporting information). The length of the micromotor clusters are ~46 μ m (Motor 1) and ~50 μ m (Motor 2), respectively. The diameter of both are ~23 μ m. The micromotor cluster originally moved in a straight line. When a static magnetic field perpendicular to motion direction was applied at 0.6 s, moving direction drastically changed. At 0.72 s, the micromotor moved in the direction consistent with magnetic field and still swam in a straight line over time. Rapid spin of 90° happened in 0.12 s under magnetic guidance, which offers high temporal resolution. The nonlinear MSD curve of Motor 1 (inset of figure 6(b)) eliminates the possibility of Brownian motion and illustrates the effective motion of the tubular micromotor clusters, because MSD change should be a straight line in the case of diffusing movement [34].

In order to explore the effect of magnetic field on micromotor speed, the speed variation of Motor 1 as a function of time is shown in figure 6(c), where the speed fluctuates around the average speed of 423 μ m s⁻¹ in 1.4 s. In comparison with the SD of 164 μ m s⁻¹ before applying a magnetic field, this value is smaller with only 59 μ m s⁻¹ when the micromotor cluster is swimming in the same direction as magnetic field. The more stable speed demonstrates that magnetic control diminishes the effect of flow disturbance on a micromotor cluster. In addition, total speed fluctuation is 38%, not larger than that of the tubular micromotor clusters demonstrated above (39%), so axial velocity values are essentially unaltered with the presence of magnetic field, which only serves to orient the micromotors longitudinally. It should be noted that, as is displayed in figure 6(c), the average speed of an Fe₃O₄/Pt nanoparticle superlattice tubular micromotor cluster (423 μ m s⁻¹) is larger than that of a Pt nanoparticle superlattice tubular micromotor cluster (~292 μ m s⁻¹) shown in figure 3(c). The reason is more microtubes are contained in the micromotor cluster utilized in figure 6.

It is the catalytic decomposition of H_2O_2 that serves to drive these microtubes in solution. Therefore, the mobility of tubular micromotors can be easily directed and wirelessly controlled under magnetic field due to their ferromagnetism. Considering its ability to swim in a low concentration of H_2O_2 , such a nanoparticle superlattice micromotor is prospective in selective biomolecule delivery.

4. Conclusion

In summary, we fabricated tubular micromotors with a carbon outer wall and monolayer Pt nanoparticles hexagonally ordered in the inner wall via an epitaxial assembly method. The benefit of this method is that it is simple, economic and completely without thin-film deposition, making it accessible for most laboratories. Then, benefiting from the geometries of clusters, the micromotor cluster exhibits high catalytic efficiency due to cooperative propulsion. H2O2 is decomposed with the existence of a Pt catalyst and produced oxygen bubbles as thrust power. The dependence of propulsion behaviour on chemical environment was demonstrated. Positive correlation was demonstrated between bubble frequency and H₂O₂ concentration, resulting in higher speed. Thanks to a dramatic enhancement of the surface area resulting from Pt nanoparticle superlattices, acceleration of the catalytic reaction enables the micromotors to move in H₂O₂ with concentration as low as 0.3%, which provides large application potential in biological environments. Various materials are available to be combined with tubular structures upon our demand under practical situation. With the integration of Fe₃O₄ nanoparticles, the motion direction of micromotors is efficiently controlled by magnetic field, revealing potential prospects of more sophisticated tasks in the future. This fabrication process extends the scope of designing routes in nano/microscale. With the capability of combining arbitrary functional materials, modified micromotor clusters hold considerable promise for future applications such as cargo delivery, environmental remediation and molecule sensing.

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