Surface roughness-induced speed increase for active Janus micromotors†

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We demonstrate a simple physical fabrication method to control surface roughness of Janus micromotors and fabricate self-propelled active Janus microparticles with rough catalytic platinum surfaces that show a four-fold increase in their propulsion speed compared to conventional Janus particles coated with a smooth Pt layer.

The use of catalytic reactions for self-propulsion of micro and nanoparticles is a well-established means to move colloidal particles in solution at low-Reynolds number.1,2 The colloids must be anisotropic in their material properties for them to generate any active propulsion. For that purpose, Janus spheres with two different faces have been fabricated, including platinum/insulator Janus micro spheres, platinum/gold bimetallic nanoparticles and nanorods, and platinum-coated microtubular jets.2–9 The propulsion in these micromotors arises from the decomposition of hydrogen peroxide (H2O2) at the platinum (Pt) surface. While a number of studies have focussed on developing new propulsion systems,10–12 different faces have been fabricated, including platinum/insulator Janus micro particles coated with a smooth Pt layer.

Increasing the surface roughness of Pt in Pt/insulator Janus particles should also lead to a higher effective area. This should consequently lead to a higher net turn-over and thus higher propulsion speeds.

Ozin et al. studied the motion of electrochemically fabricated rough bimetallic rods produced by incorporating Ludox® silica nanoparticles in the electroplating solution for bimetallic nano-rods.13 Wang et al. included carbon nanotubes into the Pt plating solution and obtained much faster speeds of the Au–CNT/Pt nanowires compared with Au–Pt ones.14 For polystyrene/Pt Janus microspheres a shift in the propulsion mechanism from diffusiophoresis to bubble propulsion was observed after chemically roughening the surface.15 Increasing the surface roughness of Pt in Pt/insulator Janus particles is, however, not straightforward. First, insulating particles do not lend themselves to direct electrochemical fabrication and typical physical vapour deposition (PVD) methods usually yield smooth surfaces. Further, bimetallic micromotors grown electrochemically have limitations in propulsion in high ionic media. This necessitates exploring different material configurations for studying microscale propulsion for which physical vapour deposition is a simple and widely used scheme.

Here, we present a facile method to obtain roughness using PVD. Commonly, Janus particles are grown by sputtering or evaporating a layer of Pt onto silica or polystyrene beads. Pt by itself does not, in general, form rough surfaces. Here we show that by first depositing an under-layer of silica before depositing the Pt introduces nanoscale roughness on the Janus particles and that this then automatically yields a rough Pt surface. We demonstrate that this leads to a four-fold speed increase compared to particles with a smooth surface. The reaction rates for catalytic propulsion were derived assuming a diffusiophoretic model of propulsion which shows a similar two to four fold increase in turnover rates for rough micromotors. The effect of roughness on catalytic activity was further verified by oxygen evolution tests and observation of the surface topology by SEM.

The morphology of thin films grown by glancing angle deposition (GLAD), a variant of PVD, where the substrate is tilted relative to the vapour flux to induce shadowed film growth, whilst permitting azimuthal rotation, depends on the deposition rate, the angle of the incident vapour and the material properties. Nanoscale...
morphology on a plane substrate can be introduced by tilting the substrate at a high angle relative to the vapour flux to induce self-shadowing during the growth.\textsuperscript{18,19} Substrate rotation under glancing angle deposition can promote columnar growth of nanostructures.\textsuperscript{18} However, metals have higher surface mobilities than (metal) oxides and will therefore diffuse on the substrate easily to form smoother surfaces compared to oxides. This effectively inhibits pure metal thin films, including Pt, from forming rough surfaces.

In this work, we have explored two different growth techniques to introduce roughness on smooth silica spheres. We first prepared a dense monolayer of silica beads (5 \(\mu\)m diameter) by drop-casting a diluted suspension of beads onto a clean silicon wafer. After drying, we placed the wafer in a vacuum PVD system. Two types of rough Pt Janus particles were grown, named R\(_1\) and R\(_2\). Both preparation methods are described below:

R\(_1\): preparation of Pt Janus micromotors under nominally normal incidence: 80 nm of SiO\(_2\) was deposited by an e-beam evaporator at 0° (normal incidence) as the first layer onto the silica beads followed by 7 nm of titanium (Ti) and 20 nm of Pt (see Fig. 1a). Ti serves as an adhesion layer. The vapour flux necessarily impinges on the curved surfaces of the silica beads with varying angles of incidence: 90° at the equator to 0° at the pole. This procedure promotes patchy growth on the particle surface (as can be seen in Fig. 1c).

R\(_2\): preparation of Pt Janus micromotors under nominally oblique angles: to stimulate growth of columnar structures on the surface of the microspheres the deposition of SiO\(_2\) was performed by tilting the substrate inside the e-beam evaporation chamber. This resulted in high angles of incidence (\(\alpha = 87°\) at the pole, Fig. 1b). In addition, the substrate was rotated about the azimuth at five revolutions per minute (Fig. 1b). Keeping the azimuthal rotation speed constant, the substrate tilt angle \(\alpha\) was continuously swept from 87° to 0° to ensure even hemispherical coverage of the surface of the microsphere (Fig. 1b). The SiO\(_2\) deposition is followed by a 7 nm layer of Ti and then a 20 nm layer of Pt, both at nominally normal (0°) incidence. It is important to note that the same amount of SiO\(_2\) is deposited in both fabrication procedures R\(_1\) and R\(_2\).

To facilitate the direct comparison with conventional fabrication of spherical Janus micromotors, we fabricated two different types of Janus particles for control purposes, named S\(_1\) and S\(_2\), which are described below:

S\(_1\): 7 nm Ti and 20 nm Pt were evaporated keeping the substrate fixed at 0° on a monolayer of silica beads (see Fig. 1a).

S\(_2\): 80 nm of Ti and 20 nm of Pt were evaporated while keeping the substrate fixed at 0° to ensure that the particles exhibit a diameter comparable to the Janus particles of R\(_1\) and R\(_2\). However, here the Pt surface is smoother than for the particles in R\(_1\) and R\(_2\) due to the higher surface mobility of the Ti adatoms. The surface-smoothness is comparable to the particles in S\(_1\).

To determine the surface morphology of the silica spheres qualitatively, the samples were examined by scanning electron microscopy (SEM). The images in Fig. 1c–f suggest the topological differences between the coated surfaces. While the top surface of R\(_1\) shows small patches of silica on the surface of the microsphere, the surface of R\(_2\) shows a wrinkled surface texture caused by self-shadowing. The coated surfaces of particles S\(_1\) and S\(_2\) have in contrast a smoother topology.

To estimate the influence of the surface roughness on the catalytic activity of the Pt decomposition of H\(_2\)O\(_2\), we have performed oxygen (O\(_2\)) evolution experiments. In order to permit quantitative measurements we chose to perform the O\(_2\) evolution tests on Si wafer-pieces (1 cm \(\times\) 2 cm) coated with smooth and rough Pt surfaces, rather than surfaces covered with the silica particles. Silica particles do not form completely close-packed monolayers causing high variability in the particle covered surface and hence the total surface area. The smooth wafers were prepared by depositing Ti (7 nm) and Pt (20 nm) at 0° as shown in Fig. 1a. The rough wafer was prepared by first depositing SiO\(_2\) under glancing angle (as shown in Fig. 1b) and subsequently coated with Ti (7 nm) followed by Pt (20 nm) at 0°. The wafers therefore mimic the surface morphology of particles R\(_2\) (rough) and particles S\(_1\) and S\(_2\) (smooth). The roughness for the particle R\(_1\) is due to the surface curvature of the silica spheres and hence cannot be mimicked by a planar wafer.

After the deposition, each wafer piece was immersed in a 100 cm\(^3\) Pyrex glass reactor containing 75 mL of 10% H\(_2\)O\(_2\) at room temperature. The detailed experimental setup to measure the evolution of gases from reactions in aqueous solutions is described elsewhere.\textsuperscript{20} Here we only give a brief description of the experimental details. The generation of O\(_2\) started as soon as the wafer covered with catalytically active Pt came into contact with the H\(_2\)O\(_2\) solution. Oxygen produced by the decomposition of H\(_2\)O\(_2\) escapes from the reactor via a silicone tube, which was then passed through a water bath at room temperature and collected in an inverted burette filled with water. The volume of the generated oxygen was deduced (at 298 K and 1 atm) from the
water level change in the burette. The maximum rates of O$_2$ evolution were determined from the maximum slope of the experimentally

determined O$_2$ generation curves. The maximum O$_2$ evolution rate for rough Pt was found to be 1.8 mmol O$_2$ cm$^{-2}$ Pt min$^{-1}$ and for smooth

Pt was 0.6 mmol O$_2$ cm$^{-2}$ Pt min$^{-1}$.

The particles were tracked for 20 s at 30 fps with a Leica optical microscope (Fig. 3) and the trajectories of 10 particles were combined to determine the average speed and the mean squared displacement (MSD) (see Fig. 4 and Videos R1, R2, S1, S2, ESI†).

At low H$_2$O$_2$ concentration (0.5%) the speeds of all particles are low and within the experimental accuracy no differences can be observed. For higher concentrations the speed of the smooth particles S1 and S2 compare well to the literature value for 5 μm particles and are comparable for all measured H$_2$O$_2$ concentrations. At 5% H$_2$O$_2$ the mean velocities between the smooth and the rough particles diverge with R1 (9 μm s$^{-1}$) and R2 (5 μm s$^{-1}$) showing, respectively a 3 and a 1.5 fold increase over particles S1 (3 μm s$^{-1}$) and S2 (2.5 μm s$^{-1}$). At 15% H$_2$O$_2$ particle R1 propels at a mean speed of 13 μm s$^{-1}$ compared to the 3 μm s$^{-1}$ of particle S1.

The mean squared displacements ($ΔL^2$) were analyzed for individual concentrations to obtain the diffusion constant, $D_{\text{diff}}$. For time scales shorter than the rotational diffusion time ($τ_r$), $ΔL^2$ can be approximated as

\[ ΔL^2 = 4D_{\text{diff}} Δt + V^2 Δt^2, \]

which is fitted for $Δt = 2$ s (Δt < $τ_r = 50$ s), where $D_{\text{diff}}$ is the diffusion constant and $V$ is the propulsion speed (Fig. S1, ESI†). The diffusion constant $D_{\text{diff}}$ is calculated by fitting eqn (1) to data of Fig. S1 (ESI†) for S1 using the error bars as weights.

The translational diffusivities of the smooth particles S1 and S2 remain close to the theoretically calculated value 0.1 μm$^2$ s$^{-1}$ for a 5 μm particle

\[ D_{\text{diff}} = k_\text{B} T/6πνR, \]

where $k_\text{B}$ is the Boltzmann constant, $T$ is temperature, $ν$ is the viscosity and $R$ is the radius of the particle. The particles R1 and R2 show a higher mean $D_{\text{diff}}$ for higher H$_2$O$_2$ concentrations reaching 3 μm$^2$ s$^{-1}$ for particle R1 (see Fig. 4b).

The self-diffusiophoretic speed can be expressed in terms of surface reaction rate $k$ as

\[ V = \frac{3πa^2}{2}kαΔ, \]

where $a$ is the hydrodynamic radius of the solute, $k$ is the reaction rate and $Δ$ is the interaction zone between the solute and the particle.

The break down of H$_2$O$_2$ can be modeled as a two-step reaction with rate constants $z_1$ and $z_2$ as,

\[ 2\text{H}_2\text{O}_2 + \text{Pt} \rightarrow z_1 \text{Pt} \cdot (\text{H}_2\text{O}_2)_2 \rightarrow z_2 \text{2H}_2\text{O} + \text{O}_2 + \text{Pt}, \]

with,

\[ k = \frac{[\text{H}_2\text{O}_2]_{\text{vol}}^2}{[\text{H}_2\text{O}_2]_{\text{vol}} + z_2/z_1}. \]

We can solve the unknown reaction rate constants $z_1$ and $z_2$ as a function of the H$_2$O$_2$ concentration by fitting eqn (3) and (5) to the speed of particles R1, R2, S1 and S2 in Fig. 4a. We assume $a = 1$ Å and $Δ = 5$ Å, and obtain the best fit line for eqn (3) to the speed data (see Fig. S2, ESI†). The experimentally determined reaction rates for different particles at 10% H$_2$O$_2$ concentrations are summarized in Table 1.

Since the difference between the different particles is primarily due to a change in surface area, the change in reaction rate and speed can serve as an indirect measure for the surface area.

Furthermore, the speed as a function of the H$_2$O$_2$ concentration saturates at higher H$_2$O$_2$ concentrations. Therefore we can choose a concentration of 10% to calculate the reaction rate and estimate the surface area enhancement effects from it. Furthermore, particle S2 with a 80 nm Ti under-layer is of the same dimension as particles R1 and R2. Hence, we can conclude that the increased reaction rate in particles R1 and R2 is caused by the surface roughness due to the nanoscale features introduced by the PVD process. From Fig. 2, we find the O$_2$ evolution for the rough Pt surface prepared using the deposition protocol for R2 is three times higher than for the smooth surface prepared by the deposition protocol for S1, suggesting that the surface area is also three times larger for the particle R2 compared with the smooth particles S1 and S2. The reaction rate at 10% H$_2$O$_2$ concentration shows a similar increase of four and two times for particles R1 and R2, respectively, compared to particles S1 and S2. Hence, we find that the increase in catalytic

Table 1  Experimental reaction rates $z_1$ and $z_2$ for R1, R2, S1 and S2 Janus particles calculated by fitting eqn (3) and (4) to the speed of the micromotors for 10% H$_2$O$_2$ concentration (Fig. S2, ESI†). We used $a = 1$ Å and $Δ = 5$ Å and solved for $z_1$ and $z_2$. We calculate the reaction rate $k$ from eqn (4) at 10% H$_2$O$_2$ concentration to compare the surface reaction rate of the different micromotors (see S4, ESI† for detailed discussion)

<table>
<thead>
<tr>
<th></th>
<th>$z_1$ (μm$^2$ s$^{-1}$)</th>
<th>$z_2$ (μm$^2$ s$^{-1}$)</th>
<th>$k$ at 10% (μm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$2.49 \times 10^{10}$</td>
<td>$1.6 \times 10^{11}$</td>
<td>$9.75 \times 10^{10}$</td>
</tr>
<tr>
<td>R2</td>
<td>$2.42 \times 10^{10}$</td>
<td>$6.40 \times 10^{10}$</td>
<td>$5.06 \times 10^{10}$</td>
</tr>
<tr>
<td>S1</td>
<td>$1.19 \times 10^{11}$</td>
<td>$2.57 \times 10^{10}$</td>
<td>$2.51 \times 10^{10}$</td>
</tr>
<tr>
<td>S2</td>
<td>$9.32 \times 10^{10}$</td>
<td>$2.50 \times 10^{10}$</td>
<td>$2.43 \times 10^{10}$</td>
</tr>
</tbody>
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of the catalyst will be higher in R₁ than in R₂ which will lead to increased propulsion speed of R₁, as is experimentally observed.

In conclusion, we have presented a fabrication scheme for making rough Pt surfaces on microsphere surfaces with PVD. We have shown that this results in a four-fold increase in the speed of the self-propelled particles compared to Janus particles that have a smooth Pt surface. Furthermore, we have characterized the surface morphology of the rough spheres and theoretically estimated the increase of surface area of the particles fabricated by glancing angle growth. The simple fabrication strategy and a high increase in catalytic surface area and propulsion speed open up a new way to control the locomotion of microscale active swimmers. It also shows the range of speed increases that are available with PVD methods. It will be interesting to apply these techniques to rolled-up tubular micromotors where the roughness may also influence the formation of bubbles.

This work was in part supported by the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement [no. 311529] and grant agreement 278213 and the DFG Research Grants Programme (Grant SA 2525/1-1) and as part of the SPP 1726 project (microswimmers, FI 1966/1-1). L.S. acknowledges the Beatriu de Pinós Program for financial support through project no. 2013 BP-B 00007.

Notes and references