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Autonomously motile catalytic nanomotors by bubble propulsion

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A bubble propulsion model based on catalyzed hydrogen peroxide decomposition and momentum change via O_2 bubbles detaching from the catalytic surface is proposed to explain the autonomous motion of catalytic nanomotors. The propelling force closely depends upon the surface tension of the liquid as well as the bulk concentration of hydrogen peroxide, and the model predictions are supported by the experimental data of Pt-coated spherical silica microbead motors. © 2009 American Institute of Physics. [DOI: 10.1063/1.3122346]

Catalytic nanomotors are artificial autonomous devises that mimic naturally occurring biological motors in the nan-ometer and micrometer length scales.¹⁻¹⁰ Several catalytic nanomotors have been realized recently through asymmetrically engineering different catalytic reactions on the backbone of nano-/microstructures, especially through the catalytic reaction of hydrogen peroxide.^{3–11} Although the overall chemical reaction is clear, the detailed physical and chemical processes for propulsion are under intense debate. Several suggested propulsion models exist including interfacial tension,⁴ self-electrophoresis,¹² diffusiophoresis,^{13–15} and bubble propulsion.^{3,5,16,17} The interfacial tension⁶ and self-electrophoresis models¹² explain how two-section nanorod nanomotors move toward the catalyst, and these two mechanisms describe experimental findings very well for the systems in question; however, other research has shown that nanomotors are propelled away from the catalyst site on a nonconducting nanorod backbone.¹³⁻¹⁸ He et al.¹⁶ has devised an experiment that clearly shows that nonconducting *L*-shaped Si/Pt nanomotors are propelled away from their catalyst site. Ismagilov *et al.*¹⁷ and Golestanian *et al.*¹³⁻¹⁵ suggested that self-mobility is the result of the diffusion of the reactants at an asymmetrical reaction site, i.e., diffusiophoresis. However, this model does not predict that the speed depends on surface tension, while previous experiments on Au/Pt nanorods show a strong dependence.⁶ Ozin *et al.*¹⁰ has experimentally shown that the motion of Au/Ni nanorods was accompanied by nanobubble evolution, but no physical details were presented. Very recently Kovtyukhova¹⁸ proposed that propulsion arises due to the pressure differences and buoyancy of the oxygen bubbles. However, those forces act only vertically to the nanomotor, while most experimental observations involve horizontal motion.⁶⁻¹⁸ In this letter we present a different bubble propulsion model based on the dynamics of bubble growth and detachment. The model predicts that the propelling force is directed away from the catalyst site and that it depends closely on the concentration of H₂O₂ and surface tension of the liquid, which agrees well with our experimental measurements.

Considering a nonconducting spherical colloid with one hemisphere consisting of a catalyst, as shown in Fig. 1, the $_{\text{catalyst}}^{\text{catalyst}}$ reaction $H_2O_2 \rightarrow H_2O+O_2(g)$ creates a higher concentra-

tion of oxygen gas on the catalyst surface in comparison to the noncatalyst surface. The concentrated oxygen coalesces to form bubbles with a critical nucleation radius R_0 on the catalyst surface. The dissolved oxygen surrounding a bubble continues to diffuse into the bubble causing it to grow while the buoyancy force and surface adhesion compete against one another. The bubble continues to grow until it reaches the detachment radius R_d and is released from the surface; the detachment results in a momentum change which induces a driving force \vec{F}_{drive} away from the catalyst surface. During the bubble detachment, the shape of the bubble is distorted and the initial detachment velocity is nonzero and has a horizontal component, as shown in Fig. 1(a) (the vertical component will be balanced by the gravitational force¹⁹). Since the catalyst is not consumed in the reaction, as a bubble detaches from the surface, a new bubble will be generated and released as long as hydrogen peroxide is present, and so the nanomotor is continuously propelled in the solution through continuous momentum change caused by a jet of oxygen bubbles. The direct observation for nanobubbles forming and being released from the surface has not occurred to our knowledge; however evidence exists for the presence of nanobubbles on rough surfaces in saturated solutions of air.⁶ These nanobubbles likely act as nucleation points for bubble growth for a locally saturated solution, and at a certain radius R_D , the bubble will detach from the surface, which is dependent upon the competition between the contact angle of a rough Pt surface and gravitational interaction. For simplicity, we assume that the bulk hydrogen peroxide concentration remains constant during the reaction and that



FIG. 1. (Color online) (a) Force and velocity schematic of a Pt-coated microsphere in a solution of hydrogen peroxide. The Pt catalyst decomposes peroxide into water and oxygen resulting in oxygen bubble formation on the surface. The detachment of the bubbles with velocity creates a driving force that is opposed by the viscosity of the fluid. Initially, the bubble is distorted as it detaches from the surface and the bubble's velocity \vec{v}_{bub} has both a vertical and horizontal component. (b) Scanning electron micrograph of a Pt-coated spherical silica microbead.

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the bubble retains its shape and volume as it detaches. Also, we only consider the speed of the bubble in the horizontal direction, as shown in Fig. 1(a). Under the steady state, dv/dt=0 and dM/dt=0 (the mass *M* of the colloid-bubble system does not change due to the balance of the catalytic reaction and bubble detachment) $F_{\rm drive}$ is due to the reaction force caused by the detachment of the bubbles, which will be balanced by the viscous drag force $\vec{F}_{\rm drag}$ to reach a constant horizontal velocity v,

$$F_{\rm drive} = N \frac{\Delta m}{\Delta t} (v_0 - v), \qquad (1)$$

where *N* is the number of bubbles detached from the surface, Δm is the mass change induced by a single bubble, Δt is the average bubble growth time until detachment, and v_0 is the initial horizontal speed of a detached bubble which may depend on the density of the surrounding fluid and acceleration of gravity. The term on the right in Eq. (1) is caused by the momentum change in the bubbles. Considering a spherical particle $F_{drag} = 6\pi\mu av$, where *a* is the radius of the colloid and μ is the viscosity of the liquid.²⁰ The speed of the colloid can be rewritten as $v = N(\Delta m / \Delta t)v_0 / [6\pi\mu a + (\Delta m / \Delta t)]$. In general, $6\pi\mu a \ge N(\Delta m / \Delta t)$ (for a sphere with a diameter of 2.0 μ m, $6\pi\mu a \sim 10^{-9}$ kg/s for water and $N(\Delta m / \Delta t)$ $\sim 10^{-22}$ kg/s according to Paxton *et al.*⁶ who measured the oxygen generation rate per area Pt catalyst in 3.7% hydrogen peroxide as 8.4×10^{-8} mol/cm² s), thus

$$v \approx N \frac{\Delta m}{\Delta t} \frac{v_0}{6\pi\mu a}.$$
(2)

Since the Reynolds number of the bubble system is very small, we neglect the effect of the fluid flow resulting from the displacement of the bubble.²¹

To estimate the bubble average detachment rate we use a simple bubble growth model. We assume that the O_2 inside a bubble is an ideal gas with a constant pressure *P* and changing volume *V* during the bubble growth, as presented by Favelukis *et al.*,²² i.e., $PV=nR_gT$ where R_g is the universal gas constant, *T* is temperature, and *n* is the molar number of O_2 . (This is a very simple assumption on bubble growth, and can be changed to other bubble growth treatments.) The bubble radius *R* obeys the following rate equation

$$\frac{dR(t)}{dt} = \frac{R_g T}{P} \frac{1}{4\pi R^2} \frac{dn}{dt} = \frac{R_g T}{P} r,$$
(3)

where *r* is the catalytic reaction rate that represents molar flux of O_2 diffusing into the bubble. Since we assume a steady-state system, the reaction rate *r* is constant, and is determined by the rate of H_2O_2 being adsorbed onto the catalyst surface as well as the catalytic reaction rate constant *k*.²³ Assuming the adsorption of the H_2O_2 follows the Langmuir isotherm, according to Ref. 23 the catalytic reaction rate can be written as

$$= \frac{k\alpha c}{1 + \alpha c}, \tag{4}$$

where *c* is the bulk concentration of H_2O_2 and α is the Langmuir adsorption constant. Combining Eqs. (3) and (4),

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$$R(t) - R_0 = \frac{R_g T}{P} \frac{k\alpha c}{1 + \alpha c} \Delta t.$$
 (5)

From Eq. (5), the average time for a bubble to grow from R_0 to R_d can be determined and the average rate of mass change is

$$\frac{\Delta m}{\Delta t} = \frac{4\pi\rho_{O_2}(R_d^3 - R_0^3)R_gT}{3P[R(t) - R_0]}\frac{k\alpha c}{1 + \alpha c},$$
(6)

where ρ_{O_2} is the density of oxygen. In Eq. (6), R_0 is determined by the saturation concentration of oxygen and the surface tension, γ , of the liquid, $R_0 = 2\gamma \kappa / (c_s - c_{eq})$, where κ is Henry's constant, c_s is the saturation oxygen concentration for bubble nucleation, and c_{eq} is the oxygen solubility.²⁴ Considering the bubble detachment radius $R_d \propto \gamma$, which has been verified numerically due to an effect of surface tension near the location of bubble detachment as the bubble deforms,²⁵ and combining Eqs. (2) and (6), we obtain an expression for motor speed v in terms of H₂O₂ concentration and surface tension,

$$v \propto N \frac{R_g T \rho_{O_2} v_0}{\mu a P} \gamma^2 \frac{k \alpha c}{1 + \alpha c}.$$
 (7)

Equation (7) predicts that the motor speed v is proportional to γ^2 and depends upon hydrogen peroxide concentration cin a complex manner. Previously, a linear dependence upon surface tension was proposed by the surface tension model⁶ and a nonlinear dependence upon concentration c has been previously reported as well.¹⁵ To test the validation of Eq. (7), we have investigated the autonomous motions of Ptcoated spherical silica colloids micromotors under different hydrogen peroxide concentrations c and various values of surface tension γ .

The Pt-coated silica microspheres were fabricated following the protocol by Love et al.²⁶ and Howse.¹⁵ The silica colloid has a diameter of $\sim 2.01 \ \mu m$ and the Pt coating was 50 nm, as shown in the SEM image in Fig. 1(b). The detached colloid spheres were then dispensed into H2O2 solutions with different concentration and surface tension, and the motions were recorded via a 1491 INi VanGuard microscope and a charge-coupled device camera. We observed the beads in the steady state, i.e., constant velocity. The surface tension of the 2% H2O2 solutions was altered by adding various concentrations of sodium dodecylsulfate and was measured by a pendant-drop method. Figures 2(a) and 2(b) show the average speed of the colloid motors for different H_2O_2 concentration c at fixed surface tension $\gamma = 72$ mN/m (the surface tension of water) and different surface tension γ for fixed c=2%. Each data point on both graphs represents the average of the average velocity for 10 microbeads taken over 10 s time interval intervals. The corresponding Brownian motion speeds have been subtracted and are also given in the two plots. The *v*-*c* plot shows a strong nonlinear relationship while the $v - \gamma$ data appears slightly exponential. Those data can be fitted quite well by Eq. (5): for the concentration dependence data, Eq. (5) can be simplified as $v = P_1 c / (P_2)$ +c), where P_1 and P_2 are two fitting parameters. The fitting curve in Fig. 2(a) gives $P_1=6.2$ and $P_2=0.5$. For low concentrations c, a roughly linear dependence exists and linear relationship between force and concentration for low concentrations has been shown,²⁷ but for higher concentrations a



FIG. 2. (Color online) Active motion of Pt-coated silica microbeads in dilute hydrogen peroxide bath. (a) The average colloid motion speed v vs the hydrogen peroxide concentration c for fixed surface tension 72 mN/m. The dashed line represents the speed of the Brownian motion. (b) The average colloid motion speed v vs surface tension γ in 2% H₂O₂. The dashed lines with symbols show Brownian motion speed for various surface tension values of which were subtracted from the data. The solid curves in both figures are the fitting results using Eq. (5).

limiting value is eventually reached. From Fig. 2(a) one can see that the motor velocity starts to level off at 2% H₂O₂ concentration. Howse *et al.*¹⁵ has suggested this phenomenon is a result of a two-stage decomposition of hydrogen peroxide by the catalyst which results in a typical Michaelis-Menten kinetics for enzymes,²³ while in our model, the reaction is naturally limited by the Langmuir isothermal (H_2O_2) adsorption). For the surface tension dependence, Eq. (5) can be reduced to $v = P_3 \gamma^2$, and the best fit in Fig. 2(b) gives $P_3=0.000$ 84, which demonstrate a very good agreement between the model and the experimental data. Since Eq. (5)links the concentration c and surface tension γ together, the fitting parameters P_1 , P_2 , and P_3 are inherently linked by the equation, $P_3/P_1 = c/\gamma^2(c+P_2)|_{\gamma=72 \text{ mN/m, } c=2\%}$. For the data shown in Figs. 2(a) and 2(b), $\gamma = 72$ mN/m and c = 2%, and the value $c/\gamma^2(c+P_2)$ is estimated to be 1.5×10^{-4} . From the fitting parameters we estimate the value $P_3/P_1 \approx 1.4 \times 10^{-4}$. This further suggests a solid agreement between theory and experiment.

In conclusion, we have presented a simple model based on oxygen bubble detachment to explain the driving force for catalytic nanomotors. We show that the propulsion is dependent upon the surface tension of the solution and on the concentration of hydrogen peroxide along with the velocity of the detached bubbles. We describe this motion through the generation of oxygen gas from the catalytic break-down of hydrogen peroxide and the formation and release of oxygen bubbles from the surface of the catalyst resulting in a change in momentum. The motion behaviors of spherical colloids have been used to test the validity of the model due to their symmetry and relatively simple and inexpensive production. The model can be applied to nanomotors of any shape by adjusting the geometric parameters. However, for systems with two metal junctions such as Au/Pt system, other propelling mechanisms may dominate the motion due to larger propelling force. Even under such a situation, the bubble induced propelling could be considered as a useful modification.

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