Measurement of driving force of catalytic nanomotors in dilute hydrogen peroxide by torsion balance

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A simple torsion balance is designed to directly determine the force generated by catalytic nanomotor nanorods. A 1 cml silicon substrate coated with $\sim 3.1 \times 10^8$ nanomotors was attached to a balancing weight and submerged into different concentrations of hydrogen peroxide. The force generated through the catalytic reaction leads to a measurable torque applied to the torsion balance. The force is on the order of $10^{-14} - 10^{-13}$ N per individual nanomotor and has a linear concentration dependence with a slope of 4.82×10^{-14} N per percentage of hydrogen peroxide in agreement with previous studies. © 2008 American Institute of Physics. [DOI: 10.1063/1.2964110]

To mimic naturally occurring biological nanomotors, autonomous catalytic nanomotors have recently attracted substantial research attention. Catalytically driven nanomotors harness energy directly from their environment. 1-3 In a solution of hydrogen peroxide, the catalyst decomposes the peroxide into water and oxygen more rapidly than the spontaneous reaction by lowering the activation energy of the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$; if the catalyst is distributed asymmetrically, an unbalanced net force or net torque will be generated and will cause the nanomotor to move.

Previous research has estimated this driving force for catalytic nanomotors. The members of the Penn State group estimate the driving force by calculating the drag force of a cylindrical bimetallic Au/Pt nanorod in hydrogen peroxide;⁴ He et al. 5 calculated the value of a Si/Pt nanorod nanomotor as $F_{\text{drive}} \approx 1.8 \times 10^{-13} \text{ N}$ using the same method. This method does not, however, account for such forces as friction, and it is an estimation based upon the dimensions of the nanomotor. Hence, it is an indirect method for measuring the force. Direct measurement is difficult due to the exceptionally small force and particle size.

Two methods could be used to directly measure the force exerted on individual nanomotors: an atomic force microscope (AFM) or a torsion balance. To measure the force with AFM, nanomotors must be attached to the AFM tip, and the force may be measured by knowing the force constant of a commercially available cantilever of which is typically around 0.1 N/m. For a force of $F \sim 10^{-13}$ N, the cantilever would experience a displacement of ~1/100th of an angstrom which is beyond the AFM detection limit. The torsion balance is a simpler setup since billions of nanomotors can be measured simultaneously. It cannot give the exact force for each individual nanomotor, but it can give a statistical estimation. Here, we directly measure this driving force with the use of a simple torsion balance; we measure the force of a large group of nanorod nanomotors in H₂O₂ that are attached to a silicon substrate, and we estimate the force due to each individual nanorod. We show that a linear relationship exists between hydrogen peroxide concentration and force.

Our torsion balance consists of metal wire suspending a solid metal piece between the top support and the base as shown in the center of Fig. 1. The center piece contains a thin metal rod of length l=15.88 cm placed through the middle of the object. Two cylindrically shaped weights that balance the system hang on both sides of the thin rod. On the side of each weight, a flat surface was cut away in order to easily attach the nanomotor substrate. A 1×1 cm² silicon substrate coated with \sim 4 μ m Si nanorods (quartz crystal microbalance reading) and a 150 nm Ag thin film³ is attached to the flat surface as shown on the right side of Fig. 1. The nanomotors were only attached on the right side of the torsion balance. A laser pointer was secured to a desk that was aimed toward a small silicon reflecting surface fixed at the center bar, and the laser light was reflected onto a ruler at a distance y=219.7 cm. Since the nanomotors are coated at an angle on the Si surface as shown in the enlarged object in Fig. 1, when this surface is submerged into the H₂O₂ solution, the direction of the driving force is perpendicular to the nanorods which will provide a horizontal force that rotates the tension wire also shown in Fig. 1. This rotation causes a deflection Δx of the laser beam in the horizontal direction. The distance Δx corresponds to the displacement on the ruler caused by the catalytic reaction. We carefully submerged the weight into a 250 ml beaker of de-ionized water, and then 30% hydrogen peroxide was drop added according to the desired concentration. The control experiment consisted of adding water instead of the concentrated hydrogen peroxide.^o

The torsion constant for the apparatus was determined through the periodic rotation of the tension wire. The torque is given by $\tau = Fd \approx k\theta$, where F is the force, d is the length of the lever arm, θ is the angle of rotation, and k is the torsion constant of the balance. Since only small angles are observed, we make the approximation: $\tan \theta \approx \theta$. By measuring the period of oscillation, we may determine the torsion constant

$$k = \frac{4\pi^2 I}{T^2},\tag{1}$$

where I is the moment of inertia. Since calculating the moment of inertia for our asymmetric center piece is impracti-

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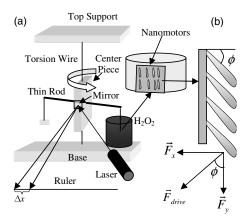


FIG. 1. (a) Schematic of the torsion balance to measure propelling force; the right balance weight has a silicon substrate with nanorod nanomotors attached. The laser light reflects off the mirror and lands upon a ruler where the displacement may be measured. (The angle is exaggerated for clarity). (b) A magnified side view of the substrate containing nanomotors deposited at an angle ϕ . The driving force is perpendicular to the line defined by the rod axis.

cal, we added the thin rod alone symmetrically through the middle of the center piece which increased the total moment of inertia to $I+\Delta I$, giving a longer period

$$T' = 2\pi \sqrt{\frac{I + \Delta I}{k}}. (2)$$

This leads to

$$k = \frac{4\pi^2 \Delta I}{T'^2 - T^2}. (3)$$

The thin rod has a moment of inertia $\Delta I = 1/3 \text{ ml}^2$, where m = 19.52 g is the mass and l = 15.83 cm is the length of the rod, and we measured the two oscillation periods: one for the center piece alone, $T = 0.46 \pm 0.06 \text{ s}$, and one for the center piece and the thin rod combined, $T' = 3.47 \pm 0.04 \text{ s}$. With these values, we determined the torsion constant for our apparatus to be $k = (3.70 \pm 0.07) \times 10^{-4} \text{ N m}$.

I. RESULTS

Previous research has shown a roughly linear hydrogen peroxide concentration dependence on velocity of Au/Pt striped nanorods.⁴ Here we show that the force applied by catalytic nanomotors is also concentration dependent. The driving force gives the measurable value Δx . Using the small-angle approximation, we have $2\theta \approx \Delta x/y$, and the force is now

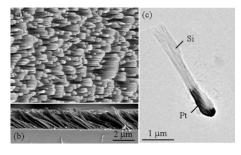


FIG. 2. (a) Scanning electron microscope top view, (b) cross-sectional view, and (c) transmission electron microscopy images of Si/Pt nanorods.

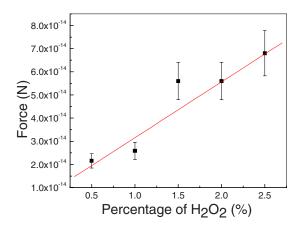


FIG. 3. (Color online) Relationship between concentration of hydrogen peroxide and force for individual nanomotors. The solid line results from linear fitting.

$$F \approx \frac{k\Delta x}{2dy}.\tag{4}$$

Equation (4) allows us to measure the force in the horizontal direction. The total number and the arrangement of the nanorod array on the surface can be estimated from the scanning electron microscope image as shown in Fig. 2. The density of the nanorods on the surface is $2.0\times10^9/\text{in.}^2$ which gives 3.1×10^8 nanorods on a 1×1 cm² area sample. Figure 2 also shows that the nanomotors are tilted at an angle of $\phi\approx55^\circ$ with respect to the surface normal, so the driving force has two components. The total driving force can be estimated as

$$F_{\text{drive}} = \frac{F_x}{\sin(\phi)}.$$
 (5)

Fig. 3 summarizes the results that show an approximately linear relationship between concentration and force with a slope of 4.82×10^{-14} N per percentage of hydrogen peroxide.

The force applied by the nanomotors depends upon the concentration of hydrogen peroxide, and the force measurements via torsion balance for catalytic nanomotors are in good agreement with previous results in the literature. Several explanations have been presented that explain the propulsion mechanism such as self-electrophoresis⁷ and diffusiophoresis. However, since we use amorphous Si as the backbone of the nanomotors, and Si does not have good electric conductivity, the mechanism in our nanomotor design is unlikely to be self-electrophoresis. The detailed mechanism is still being investigated.

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