Rational Design and Synthesis of Catalytically Driven Nanorotors

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Chemically and catalytically powered nano-objects are a fascinating area of research. They have the potential to facilitate the development of nanomechanical devices that could find utility in microfluidics and drug delivery.1–11 Over the past 3 years, several groups have studied how the catalytic decomposition of H2O2 by multicomponent segmented nanorod structures (Pt–Au, Ni–Au) can drive nanomechanical systems.10–20 Most of the systems studied thus far, such as in the work of Mano et al., Wang et al., Paxton et al., and Kline et al. have involved chemically powered linear motion,10,11,13,15,18 although a couple of examples involve the spinning of structures tied to a surface at one end of a two-component, two-segment nanorod.16 In another example, Catchmark et al. demonstrated rotational movement in a conventionally microfabricated microgear based on the same catalytic reactions, and Chang et al. demonstrated macro-object rotation via linked diodes.6,21 Last, bent structures have been prepared by He et al. by “dynamic shadowing growth” that allow one to realize “boomerang-like” structures composed of Pt and Si. These impressive catalytically powered structures are capable of spinning, but the fabrication approach used to generate them is complex, low yielding in terms of functional structures, and does not provide fine control over the architectural parameters (compositional blocks, length, diameter) important to the controlled movement of such structures.22

Controlling the asymmetric forces involving these H2O2 driven nanomotors is a major challenge. This control, which is essential for achieving a stable torque on these nano-objects, requires a precise method for adjusting the nanorod segment dimensions, compositions, and locations. On-wire lithography (OWL) has emerged as a method for tailoring the architecture of nanorod materials on the sub-5 nm to many micrometer length scale.23–25 This approach, which is based upon template-directed synthesis,26–29 not only allows one to control the composition of different segments along the long axis of the rod, but also allows one to coat one face of multicomponent rod structures with a desired material. We hypothesized that this capability would allow us to synthesize a set of structures with the proper compositional blocks and asymmetry to realize a new class of catalytically powered nanorotors (NR). As proof-of-concept, we synthesized Au–Pt–Au three-segment nanorods (diameter = 360 nm; first Au section length = 1.67 μm, Pt section length = 3.33 μm, second Au passivating section length = 20 nm) coated on one face with a Au/Cr bilayer (10 nm Cr/40 nm Au) via OWL (Scheme S1, see Supporting Information). These nanostructures leave only one side of the Pt segment exposed (Scheme 1A).

After synthesizing these structures, we studied their movement driven by the catalytic decomposition of H2O2. In a typical experiment, 10 μL of an aqueous suspension of NRs (containing 1 × 105 rotors) was mixed with 1 mL of 3% H2O2. A droplet of the mixture was promptly placed on a glass bottom dish and characterized by dark-field optical microscopy. Of the 500 NRs studied, 95% were actively rotating while the remaining 5% exhibited either random or linear motion, possibly due to structural defects generated during synthesis. This rotation of the NRs was recorded to determine the direction and speed of rotation (video S1, see Supporting Information).

In a representative sample of the Au1.67Pt3.33Au0.02 NRs, one can distinguish the Au and Pt sections based upon color and contrast (Figure 1). The yellow ends are the gold segments and the gray section is Pt. Time lapse dark field microscopy experiments show that a full turn of a NR is completed in 2.53 s corresponding to a rotation speed of 23.7 rpm, Figure 1. Note that the NRs can rotate in both a clockwise and counterclockwise direction, and the speed increases with increasing H2O2 concentration up to 3% H2O2. At or above this concentration the reaction is limited by Pt surface area rather than peroxide concentration.

There have been two general classes of mechanisms proposed for nanorod locomotion. They can be differentiated by the direction in which the nanorod moves. In the first class, catalytic H2O2 decomposition at a two component Au–Pt or Au–Si rod is proposed to explain cases in which the nanorod is pushed in the direction defined by the gold (or Si) end being the leading edge (the so-called “recoil mechanism”).16,22 In the second class, the localized product concentration from H2O2 decomposition creates either an electrofluidic gradient or an interfacial tension that results in the rod being pulled in the opposite direction toward the Au end.3,11,13,18,21 Since the evaporated gold backings in our NRs are the leading edges during rotation, this second class of mechanisms does not fit our system (Video S2, Figure S3, see Supporting Information). To determine if the electrofluidic mechanism described above was in play in this system, we added NaNO3 to the solution (final concentration = 0.33 mM). The NaNO3 has been proposed to screen the NR’s ζ-potential, which should minimize contributions defined via the electrofluidic mechanism.30 The NR

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The whole structure is resisted by the fluid nearly uniformly across a cross-section of the nanorod, resulting in a net rotation. The movement of the nanorod is propelled by the gas evolution, which propels the structure, resulting in a net rotation. The movement of the whole structure is resisted by the fluid nearly uniformly across the nanorod length and diameter of the rod and introduces the Au backing to the Au nanorods. When the applied torque is considered in the driving force of the motion in this catalytically driven nanomotor has a quasi-parabolic relationship with the Pt/Au ratio. The maximum rotation speed takes place very close to the Pt/Au ratio of 2.0. This work is a significant step toward systematic design of nanorods with more complex movement patterns.

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Supporting Information Available: Experimental details and optical microscopy video images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. Science 2005, 310, 80–82.
(22) He, Y.; Wu, J.; Zhao, Y. Nano Lett. 2007, 7, 1369–1373.

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