Self-Propelled Carbohydrate-Sensitive Microtransporters with 'Built-in' Boronic-Acid Recognition for Isolating Sugars and Cells

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SI Video Captions

SI Video 1 *(available online as file ja306080t_si_002.mpg).* A PAPBA/Ni/Pt microrocket carrying multiple yeast cells (in 5% H_2O_2 containing 1.5% NaCh).

SI Video 2 *(available online as file ja306080t_si_003.mpg).* Motion of a PAPBA/Ni/Pt microrocket in human serum (in 5% H_2O_2 containing 1.5% NaCh).

SI Video 3 *(available online as file ja306080t_si_004.mpg).* A PAPBA/Ni/Pt microrocket captures, transports and releases the yeast cell (corresponding to Figure 2).

SI Video 4 *(available online as file ja306080t_si_005.mpg).* A PAPBA/Ni/Pt microrocket in suspended *S. aureus* media (corresponding to Figure 3A).

SI Video 5 *(available online as file ja306080t_si_006.mpg).* A PEDOT/Ni/Pt microrocket in suspended yeast cells media (corresponding to Figure 3B).

SI Video 6 *(available online as file ja306080t_si_007.mpg).* A PAPBA/Ni/Pt microrocket captures and transports a glucose-incubated PS media microsphere (in 3% H_2O_2 and 1.5% NaCh).

SI Video 7 *(available online as file ja306080t_si_008.mpg).* The motion of PAPBA/Ni/Pt microrocket in glucose-incubated PS and different 'control' solutions: PS, sucrose-incubated PS, lactose-incubated PS and PANI/Ni/Pt microrocket in glucose-incubated PS media.

Experimental Section

Materials

3-Aminophenylboronic acid, sodium sulphate, sodium chloride, sodium carbonate and D-(+) glucose, β-D(-) fructose, sucrose, lactose and human male AB plasma serum were purchased from Sigma-Aldrich Chemical Inc. (St Louis, MO). Polystyrene beads (PS) (2 μm) was obtained from Polysciences, Inc. (Warrington, PA). Other chemicals were in analytical grade and supplied from Sigma-Aldrich Chemical Inc. (St Louis, MO). The yeast cell strain used in the experiments was a derivative of W303 genome strain.

Equipments

Template electrochemical deposition of microtubes was carried out with a CHI 661D potentiostat (CH Instruments, Austin, TX). Scanning electron microscopy (SEM) images were obtained with a Phillips XL30 ESEM instrument, using an acceleration potential of 20 kV. The SEM images were taken shortly after the microtube samples in ethanol suspension freshly dried up. Videos are captured by an inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a 20x objective, a Hamamatsu digital camera C11440 using the NIS-Elements AR 3.2 software.

Fabrication of PAPBA/Ni/Pt microrockets

The PABPA/Ni/Pt microtubular rockets were prepared using a common template-directed electrodeposition protocol. The Cyclopore polycarbonate membranes, containing 2 μm diameter (Catalog No 7060-2511; Whatman, Maidstone, U.K.) conical-shaped micropores, were employed as the templates. A 75 nm gold film was first sputtered on one side of the porous membrane to serve as working electrode using the Denton Discovery 18 system. A Pt wire and an Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. The membrane was then assembled in a plating cell with an aluminum foil serving as a contact. PAPBA-functionalized microrockets were then prepared by controlling electrochemical polymerization in an aqueous acidic solution containing 3-aminophenylboronic acid (APBA) (80 mM), sodium sulphate (0.3 M) and 0.125 M HCl. The electropolymerization was carried out at +0.9 V (vs. Ag/AgCl) using a charge of 0.6 C. Subsequently, a platinum-nickel alloy layer was plated at -0.5 V for 50 s (a thin Pt layer), -1.0 V for 300 s (Pt-Ni alloy, mostly Ni) and -0.5 V for 120 s (inner Pt layer) using a 1:1 (v:v) mixed solution of a commercial platinum solution and a nickel plating solution containing 20 g L^{-1} $NiCl_2 \cdot 6H_2O$, 515 g L^{-1} $Ni(H_2NSO_3)_2 \cdot 4H_2O$, and 20 g

L^{-1} H_3BO_3. Throughout the text we will refer to the resulting PAPBA/Pt/Pt-Ni Alloy/Pt microtubes as PAPBA/Ni/Pt microrockets.

Incubation of PAPBA/Ni/Pt microrockets with glucose/disaccharide incubated PS

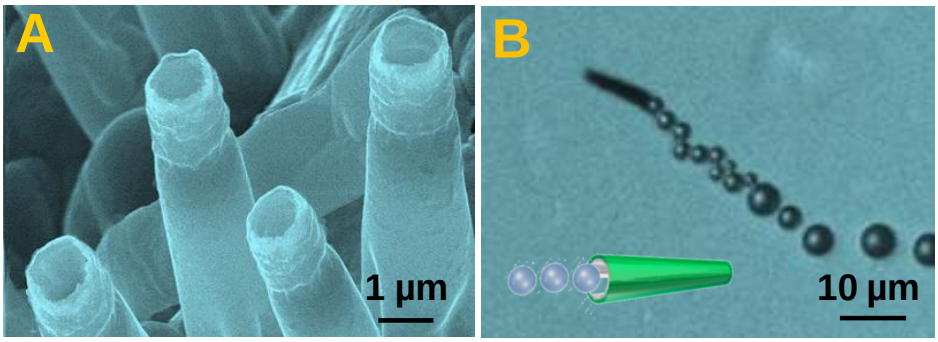
50 µL PS (2 µm diameter) dispersion and 50 µL glucose solutions (7 mM prepared in pH 8.5 phosphate buffer) were incubated overnight. Then, the solution was washed and was retained in phosphate buffer. The PS/glucose solution was used for demonstrating the sugar pick-up process by PAPBA/Ni/Pt microrockets.

50 µL PS (2 µm diameter) dispersion and 50 µL sucrose or lactose solutions (70 mM prepared in pH 8.5 phosphate buffer) were incubated overnight. Then, the solution was washed and kept into phosphate buffer. The PS/disaccharide solution served as negative control to check any binding on PAPBA/Ni/Pt microrockets.

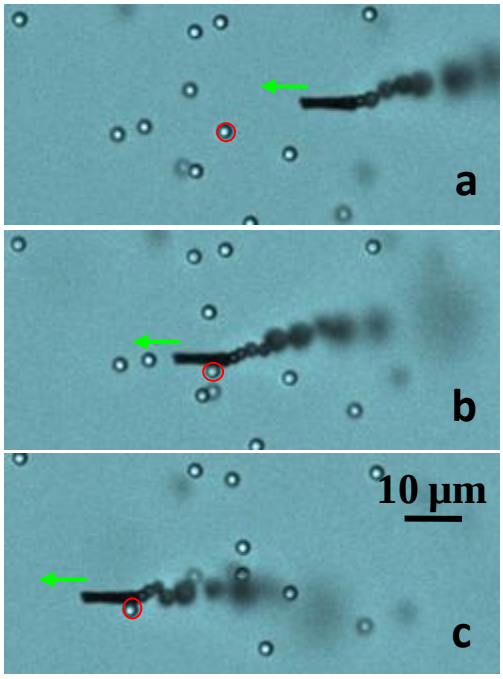
To prevent potential nonspecific binding of these microspheres in pure water, a 50 mM phosphate buffer solution (pH 8.5, including 150 mM NaCl) was used in these particle experiments.[1] No apparent change in the target binding efficiency was observed during the experiments, indicating no apparent degradation of PAPBA recognition layer by the peroxide fuel.

UV-vis spectroscopy studies

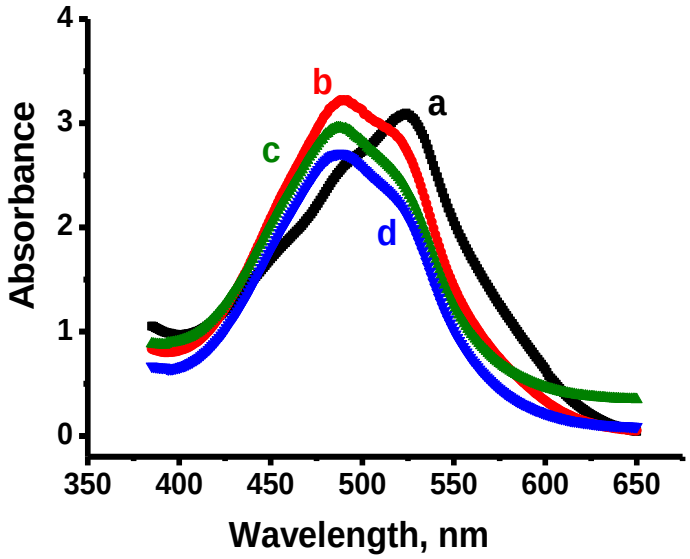
Spectroscopic studies were carried out with Shimadzu UV-VIS Spectrophotometer UV-2450. Alizarin Red S was dissolved in phosphate buffer pH 8.2.



SI Figure 1. a) SEM images of bilayer PAPBA/Pt microrockets. b) The continuous motion of PAPBA/Ni/Pt microrocket in human serum (in the presence of 5% H_2O_2 containing 1.5% NaCh).



SI Figure 2. The PAPBA/Ni/Pt microrocket approaching (a), capturing the first (b) transporting a glucose-loaded microsphere (c) (in 3% H_2O_2 and 1.5% sodium cholate, based on SI Video 6).



SI Figure 3. Absorption spectra of a) ARS; b) ARS+PABPA/Ni/Pt microrockets; c) ARS+PABPA/Ni/Pt microrockets+5 mM glucose; d) ARS+PABPA/Ni/Pt microrockets+10 mM glucose (phosphate buffer pH 8.2).

References

(1) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem. Int. Ed.* 1999, *38*, 3666.