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Orthogonal navigation of multiple visible-light-driven artificial microswimmers

Jing Zheng, Baohu Dai, Jizhuang Wang, Ze Xiong, Ya Yang, Jun Liu, Xiaojun Zhan, Zhihan Wan & Jinyao Tang

Nano/microswimmers represent the persistent endeavors of generations of scientists towards the ultimate tiny machinery for device manufacturing, targeted drug delivery, and noninvasive surgery. In many of these envisioned applications, multiple microswimmers need to be controlled independently and work cooperatively to perform a complex task. However, this multiple channel actuation remains a challenge as the controlling signal, usually a magnetic or electric field, is applied globally over all microswimmers, which makes it difficult to decouple the responses of multiple microswimmers. Here, we demonstrate that a photoelectrochemically driven nanotree microswimmer can be easily coded with a distinct spectral response by loading it with dyes. By using different dyes, an individual microswimmer can be controlled and navigated independently of other microswimmers in a group. This development demonstrates the excellent flexibility of the light navigation method and paves the way for the development of more functional nanobots for applications that require high-level controllability.
The design and fabrication of microswimmers with flexible manipulation capability and excellent biocompatibility may have a profound impact on people’s lives due to its potential applications in healthcare, manufacturing, and environmental remediation. Over the past decade, varieties of artificial microswimmers have been developed which generate propulsion thrust by harvesting energy from magnetic field, electric field, acoustic wave, light or chemical fuels. On the other hand, to control the migration of the microswimmers remotely, an external control signal is required to align the microswimmers to the desired orientation. Currently, most of the demonstrated microswimmers rely on the external magnetic field for direction control due to its simplicity and the excellent biological tissue penetration. However, one challenge facing the magnetically driven microswimmer is that since it is difficult to confine the magnetic field in a small area, a global field is applied over all microswimmers within the interested area, which makes it difficult to address the microswimmer individually and realize multi-channel actuation. This multi-channel capability is particularly important for the long-envisioned non-invasive surgery as well as some micromanipulation application where many conceived operations can only be accomplished by the cooperative maneuvers of many individually addressed microswimmers. Recently, some limited success of the multi-channel actuation of magnetic microswimmers were proposed/demonstrated by introducing another degree of freedom to differentiate magnetic actuators such as the different mechanical actuation, electric field, light or chemical fuels. The multichannel actuation strategy is a general method for multichannel actuation without the requirement for specialized substrate or minimum swimmer–swimmer distance. We expected that by applying different dyes with narrower absorption band and near-infrared activity, the microswimmers with more orthogonal channels and near-infrared activity could be realized. Furthermore, our strategy can also be applied to prepare microswimmers with broadband visible light sensitivity, which can be used as the solar-powered microswimmer for environmental remediation.

**Results**

Fabrication and characterizations of the microswimmers. Large-scale Si/TiO$_2$ nanotree was synthesized by modified metal-

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**Fig. 1** Schematic diagram and structural characterizations of the microswimmers. a) False-colored scanning electron microscope image of the dye-sensitized Janus nanotree with TiO$_2$ nanowire branches and silicon nanowire trunk (scale bar: 10 μm). b) Schematic diagram of the dye-sensitized microswimmer driven by photoelectrochemical reaction with the numerically simulated charge distribution (color map). The length of the arrow is normalized and does not represent the flow magnitude. c) The photograph of the dye alcoholic solutions and the corresponding dye-sensitized nanotree samples. d) The confocal fluorescence mapping images of the dye-sensitized microswimmers, which show that all three dyes are selectively loaded onto the TiO$_2$ nanowire surface (scale bar: 5 μm)
assisted electroless chemical etching process followed by TiO2 nanowire hydrothermal growth based on our previous study46,47. The scanning electron microscopy (SEM) image shows that the as-prepared nanotrees are composed of 6-μm-long silicon tails and 4-μm-long TiO2 nanowire heads with 2.5 μm diameter (Fig. 1a). To extend the photosresponsivity of the nanotree microswimmer to visible range, three sensitizing dyes N719 (cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylyato) ruthenium(II) bis(tetrabutylammonium), as received from Dynamos, Inc.) and from Solaronix), D5 (3-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid, as received from dynanox, Inc.) and SQ2 (5-carboxy-2-[3-[(2,3-dihydro-1,1-dimethyl-3-ethyl-1H-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene)methyl]-3,3-dimethyl-1-octyl-3H-indolium, as received from Solaronix) were employed to code the microswimmers with green, blue and red light sensitivity, respectively. In typical DSSCs, the iodide/triiodide (I−/I3−) redox couple is utilized to shuttle the charge from anode to cathode. Recently, it is discovered that the hydroquinone/benzoquinone (QH2/BQ) can also serve as an effective redox shuttle for high-efficiency DSSCs46, which can also be applied to our microswimmer system. As shown in Fig. 1b, our nanotree is immersed in QH2/BQ mixture aqueous solution and functions as a miniaturized DSSCs, where the dye-sensitized TiO2 branches serve as the photoanode and the silicon nanowire trunk serves as the photocathode. Upon illumination, the dye molecules absorb energy from the incident light and transfer the photoexcited electrons to TiO2 nanowires and promote the oxidation of QH2 into BQ which releases H+ and makes the local solution around the TiO2 nanowires slightly positively charged. Meanwhile, the photoexcited electrons in silicon nanowire reduced the BQ back to QH2 which releases OH− and makes the local solution around the silicon nanowire slightly negatively charged. This unbalanced distribution of the charged H+ and OH− ions is simulated with commercial numerical software (COMSOL Multiphysics, See the Methods) and shown in Fig. 1b. The nanotree propels by this self-generated electrical field via electrophoresis mechanism as reported previously46. A nanotree migration speed (SQ2 sensitized microswimmer under 660 nm light illumination with an intensity of 328 mW·cm−2) of ~0.8 μm·s−1 can be calculated by the fluid speed simulation using the method developed by Solomentsev et al.47,48 (see the Methods). Particularly, due to the selective chemisorption of the carboxylate acid (−COOH) group on TiO2 surface, the organic dye is covalently loaded on the nanotree (Fig. 1c) by simply immersing the synthesized nanotrees into the dye alcoholic solutions. The selective anchoring and distribution of dyes were confirmed by the confocal fluorescence images (Carl Zeiss LSM 710 NLO) of the dye-sensitized nanotree. As shown in Fig. 1d, all dyes are selectively anchored on the TiO2 surface and will not affect the photoelectrochemical properties of silicon nanowire.

Wavelength and intensity-dependent migration. Since the dye-sensitized microswimmer is propelled by the light absorption of dye molecules, the spectral response of the microswimmer is determined by the spectral response of the corresponding dye-sensitized solar cell. The external quantum efficiency (EQE) of the dye-sensitized nanowire solar cell with corresponding dyes was measured based on previously reported procedure49 (see the Methods and Supplementary Fig. 1) and compared with the spectral response of the microswimmer. As shown in Fig. 2a, the peak EQE for D5, N719 and SQ2 sensitized solar cell are ~0.45, ~0.510 and ~0.610 nm respectively. To quantify the spectral response of the dye-sensitized microswimmers, the migration speeds of the microswimmers are quantified while a supercontinuum laser coupled with the variable linear filter was utilized as the wavelength tunable illumination source. For all measurement, the
Fig. 3 The orthogonal photoresponse of the dye-sensitized microswimmers. a The superimposed image of the sequential frames shows the migration of D5 and SQ2 sensitized microswimmers under blue (475 nm) and red (660 nm) light alternating illumination (Supplementary Movie 1). Inserts: the molecular structures of D5 and SQ2 dye. b The migration speed of D5 (blue curve) and SQ2 (red curve) sensitized microswimmers in a under the alternating light illumination.

Orthogonal navigation of the dye-sensitized microswimmers. As we demonstrated previously, the nanotree-based microswimmer can not only be propelled but also be navigated by light with the self-shadowing effect of the nanotree. The multichannel controllability can be achieved with the light of different wavelength if the orthogonal spectral response of the microswimmers can be obtained. Here we demonstrate the independent navigation of multiple dye-sensitized microswimmers based on D5 and SQ2 dyes. This general strategy may also be extended to other organic dyes and inorganic quantum dots sensitized system to realize different spectral response of the microswimmer.

A customized stage is utilized to study the navigation ability of the D5 and SQ2 dye-sensitized microswimmers where four independently controllable red (660 nm) and blue (475 nm) LEDs are mounted at the four edges of the stage (see the Methods and Supplementary Fig. 2) to illuminate the microswimmers from controllable direction. As shown in Fig. 4a, the D5 and SQ2 dye-sensitized microswimmers are subjected to the side illuminations of 475 and 660 nm wavelength light spontaneously to control their orientation, while the 550 nm green illumination from the microscope objective is utilized for imaging which has minimum interference with both D5 and SQ2 sensitized microswimmers.

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D5 sensitized microswimmer irrespective of the red illumination direction. During this process, the orientation of SQ2 loaded microswimmer is locked by the illumination direction of 660 nm red light and does not show any rotation with the blue light source. Comparatively, the fixed 475 nm blue illumination with rotating 660 nm red illumination only drive the rotation of the SQ2 sensitized microswimmer without affecting the alignment of the D5 sensitized microswimmer (Fig. 4c and Supplementary Movie 2). These experiments demonstrated that the dye-sensitized microswimmer could indeed be controlled independently. As shown in Fig. 4d and Supplementary Movie 3, the D5 sensitized microswimmer (blue) and the SQ2 sensitized microswimmer (red) are simultaneously propelled and steered with 475 and 660 nm illumination and spell ‘r’ and ‘b’, respectively. With this simple dye-sensitize strategy, in principle, the microswimmer can be coded with an arbitrary spectral response by controlling the absorption spectrum of the adsorbed dyes. With the fruitful knowledge of the well-developed DSSCs and readily developed varieties of dyes and quantum dots, further improved functional microswimmers are expected. For example, more orthogonal channels for the microswimmers can be developed based on tandem dye-sensitized solar cell50. Furthermore, the near-infrared sensitive microswimmers can be developed on infrared dyes51 which are preferred for biological application due to the larger optical penetration depth in tissues.

Discussion
In summary, we have successfully designed and demonstrated the visible light driven dye-sensitized artificial microswimmers based on Janus TiO2/Si nanotree structure. The spectral response of the microswimmer is determined by the absorption spectrum of the loaded dye on the TiO2 nanowires. By properly selecting the dyes with orthogonal absorption spectrum and the corresponding illumination wavelength, the sensitized microswimmers can be independently propelled and navigated. This orthogonal multi-channel navigation capability of the microswimmers represents a major step towards the more controllable microswimmers. More advanced nanorobot may be developed by integrating multiple independent controllable parts for complexed functions.

Methods
Fabrication procedure of dye-sensitized nanotree forest. The large-scale nanotree forest was synthesized by modified metal-assisted electroless chemical etching process followed by TiO2 nanowire hydrothermal growth. Prior to the dye adsorption, the prepared Janus TiO2/Si nanotree forest was sintered in air under 450 °C for 30 min, and the platinum nanoparticles were loaded on the surface of the silicon trunk by dipping the prepared sample into the mixture solution of 0.5 mM chloroplatinic acid (Sigma-Aldrich) and 0.5 M hydofluoric acid (Sigma-Aldrich) for 1.5 min for 6 cycles.

Three sensitizing dyes N719 (cis-diisothiocyano-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), as received from Solaronix), D5 (3-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid, as received from dyenamo, Inc.) and SQ2 (5-carboxy-2-[(2,3-dihydro-1,1-dimethyl-3-ethyl-1H-benzo[e]indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene[methyl]-3,3-dimethyl-1-oxyl-3H-indolium, as received from Solaronix) were employed to sensitize the as prepared nanotree forests. 2D models were adapted from the bimetallic motor system. Hydro-quinone/benzoquinone (QH2/BQ) system was taken as a representative system for oxidation and reduction, the samples were immersed in a 0.5 mM ethanolic solution of dye for 1.5 min for 6 cycles.

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Charge distribution and electric field simulation. Ion-induced charge distribution and fluid speed were simulated using the commercial COMSOL Multiphysics package. 2D models were adapted from the bimetallic motor system. Hydro-quinone/benzoquinone (QH2/BQ) system was taken as a representative system for numerical study. Cations (H+) and anions (OH−) are generated at TiO2 (anode)
and Si (cathode) surfaces, respectively and are further distributed by the diffusion (Supplementary Table 1), convection and migration of ions (Equation Eq. (1)): 
\[ V_0 = V_C - V_D + \frac{zF \Delta C(V_C - V_D)}{RT} \]  
(1)

where \( V_0 \) is the flux of ion \( i \), \( F \) is the Faraday constant, \( \phi \) is the electrostatic potential, \( R \) is the gas constant, \( T \) is the temperature and \( C_D \) and \( C_T \) are the concentration, diffusion coefficient, and charge of species \( i \), respectively. The \( H^+ \) and \( OH^- \) will react into \( H_2O \) quickly when they combine with each other.

The electric field \( E \) (\( E = -\nabla \phi \)) in Eq. (1) is calculated using the Poisson equation:
\[ -\varepsilon_0 \varepsilon R \nabla^2 \phi = \rho = F(Z, \xi, z + Z, \varepsilon_c) \]  
(2)

where \( \varepsilon_0 \) is the vacuum permittivity and \( \varepsilon_r \) is the relative permittivity of water, \( Z_r = 1 \) and \( \varepsilon = 1 \), \( \rho \) is the volumetric charge density, \( F \) is the Faraday constant and \( C_D \) the concentration of the \( \text{H}^+ \) and \( \text{OH}^- \), respectively. The boundary condition was adopted according to the zeta potential of \( \text{TiO}_2 \) (\( -10 \pm 2 \text{mV} \)) and Si nanowire (Si surface \( -20 \text{mV} \)). The ion fluxes generated on the anode and cathode surfaces are calculated based on SQ2 sensitized microswimmer illuminated by 660 nm light at 32 mW cm\(^{-2}\) illumination power and the EQE measured from the DSSCs (Supplementary Fig. 1), which is corresponding to the photocurrent density of \( \text{TiO}_2 \) (184 A m\(^{-2}\)) [Eq. (3)].
\[ \text{Intensity} \frac{\text{blue}}{\text{red}} = \frac{\text{Intensity} \frac{\text{D5}}{\text{SQ2}}}{} = 0.92 \pm 0.02 \text{dB} \]  
(3)

The light-intensity-normalized migration velocity (LINMV) (95% confident interval) under blue and red light illumination are as follow: 
\[ \text{Intensity} \frac{\text{blue}}{\text{red}} = 1.0 \pm 0.05 \text{mms}^{-1} \]  
(4)

Thus, the minimum S/I (interference tolerance) for D5 and SQ2 sensitized microswimmers are \(-15.63 \pm 15.35 \text{dB}\), respectively (Eq. (5)).
\[ \text{Interference tolerance} = 10 \log_{10} \left( \frac{\text{Intensty} \frac{\text{D5/ SQ2}}{\text{eye}}}{\text{eye}} \right) = -15.35 \pm 15.63 \text{dB} \]  
(5)

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
J.Z. and B.D. contributed equally to this work. J.Z., B.D. and J.T. conceived and designed the experiments. J.Z., B.D., X.Z. and J.T. fabricated the devices. J.Z. and B.D. performed the measurements and analysis of the data. Z.X., J.W. performed the numerical simulation. J.Z. and Y.Y. took the confocal fluorescence mapping images, J.Z. and J.T. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information
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