Multiwavelength-Steerable Visible-Light-Driven Magnetic CoO–TiO$_2$ Microswimmers

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**ABSTRACT:** While current light-driven microswimmers require high-intensity light, UV light, or toxic fuels to propel them, powering them with low-intensity UV-free visible light without fuels is essential to enable their potential high-impact applications. Therefore, in this study, a new material for light-driven microswimmers in the form of CoO is introduced. Janus CoO–TiO$_2$ microswimmers powered with low-intensity, UV-free visible light inside water without using any toxic fuels like H$_2$O$_2$ is proposed. The microswimmers show propulsion under full spectrum of visible light with 17 times lower intensity than the mean solar intensity. They propel by breaking down water into oxygen and oxide radicals, which enables their potential applications for photocatalysis and drug delivery. The microswimmers are multiwavelength responsive, from the ultraviolet to the infrared region. The direction of swimming changes with the change in the illumination from the visible to UV light. In addition to being responsive, they are wavelength steerable and exhibit inherent magnetic properties enabling magnetic steering control of the CoO–TiO$_2$ microswimmers. Thus, these microswimmers, which are propelled under low-intensity visible light, have direction-changing capability using light of different wavelengths, and have steering control capability by external magnetic fields, could be used in future potential applications, such as active and local cargo delivery, active photocatalysis, and hydrogen evolution.

**KEYWORDS:** microswimmers, light-driven, photocatalysis, cobalt monoxide, titanium dioxide

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**INTRODUCTION**

Chemically powered synthetic microswimmers have been inspired by natural biological motors for propulsion and control.\textsuperscript{1–3} Their propulsion can be controlled by modulating the type of chemical reactions, such as catalytic or enzyme microswimmers. Also, light is an excellent power source for microswimmers, and light-driven microswimmers have shown tremendous potential for various applications, such as environmental remediation,\textsuperscript{4} drug delivery,\textsuperscript{5} and self-assembly.\textsuperscript{6} Photocatalytic semiconductor materials have been mainly used to design light-driven microswimmers.\textsuperscript{6} The most commonly used semiconductor photocatalysts in light-driven microswimmers are titanium dioxide (TiO$_2$),\textsuperscript{7,8} and its various modifications,\textsuperscript{9,10} ZnO,\textsuperscript{11} AgCl,\textsuperscript{12,13} BiOCl,\textsuperscript{14} BiVO$_4$,\textsuperscript{15} Sn,\textsuperscript{16} TiO$_2$,\textsuperscript{17} Cu$_2$O,\textsuperscript{18} Cu,\textsuperscript{19} CuO,\textsuperscript{20} CdS,\textsuperscript{21} CdSe,\textsuperscript{22,23} alloy,\textsuperscript{24} and Fe.\textsuperscript{25} Most of them are active only in the ultraviolet (UV) region, while the microswimmers active in the visible light region require redox shuttles or other fuels to propel them. From these photocatalysts, Ag/AgCl-based microswimmers only have shown relatively high swimming speeds under visible-light illumination.\textsuperscript{13} When it comes to their potential applications, such as environmental remediation, they seem to be quite limited for the selection of the light source. Moreover, most of light-driven microswimmers often rely on using H$_2$O$_2$ to enhance their propulsion.\textsuperscript{26} The addition of H$_2$O$_2$ causes many potential pitfalls in their practical applications due to their inherent toxicity.

Cobalt monoxide (CoO) can be an excellent candidate to create light-driven microswimmers. It has one of the highest overall photocatalytic efficiency (≈5%) under visible light\textsuperscript{27} and has the ability to break down water into both hydrogen (H$_2$) and oxygen (O$_2$).\textsuperscript{28} It also has the ability to break down water without the presence of any external reagents or donors. Initially, only CoO nanopowders showed increased catalytic activity, while CoO micropowders was found to be very less active in the presence of light.\textsuperscript{29} Then, CoO microparticles with the specific crystallographic lattice structure have recently been found to be active in the presence of visible light,\textsuperscript{30,31} unlike TiO$_2$ absorbing photons in the UV region.\textsuperscript{32} Although the UV photons have more energy, they are not so widespread in sunlight. CoO is known to absorb light mostly in the visible and near-infrared (NIR) regions.\textsuperscript{33} To increase the activity of micron-scale CoO micropowders, a CoO–TiO$_2$ heterojunction is used.\textsuperscript{34,35} The

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CoO−TiO₂ microswimmers can have both visible and UV light absorption capabilities. Such a property is due to the broader energy gap of the heterojunction, hence absorbing light of different wavelengths.

In this work, we show that photocatalytic composite CoO−TiO₂ Janus microswimmers can be propelled by both low-intensity visible and UV light. To the best of our knowledge, the use of CoO for applications to microswimmers is reported for the first time. In comparison with other light-driven microswimmers in the literature, these microswimmers have one of the highest swimming speeds under UV-free visible spectrum and low-intensity light in the absence of any external fuels. We also demonstrate that the propulsion direction can be also changed with the application of light of different wavelengths, where CoO is reactive to visible light and TiO₂ is reactive to UV light, creating another type of steerable microswimmers based on the incident wavelength, without the need for phototaxis to steer them. The use of wavelength-based steering enables potential applications of CoO−TiO₂ microswimmers in steerable navigation and cargo delivery. In addition, these microswimmers can be steered by external magnetic fields due to the magnetic properties of CoO, without the deposition of an additional magnetic layer during the fabrication process.

 RESULTS AND DISCUSSION

Characterization of CoO−TiO₂ Microswimmers. The CoO−TiO₂ microswimmers are fabricated by depositing a TiO₂ thin film on Co₃O₄ microparticles to create Janus particles and subsequent annealing under controlled conditions to form an annealed and crystallized Janus CoO−TiO₂ microswimmer. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), electron energy-loss spectroscopy (EELS), and diffuse-reflectance spectroscopy (DRS) are used to characterize the structure, crystallinity, and absorption spectra of the fabricated microswimmers. SEM and energy-dispersive X-
ray spectroscopy (EDS) are used to inspect their shape and element distribution. Additionally, XRD and XPS are used to confirm the formation of a CoO core. Their optical properties are characterized by EELS and DRS. A schematic of the Janus CoO–TiO2 microswimmer is shown in Figure 1a. The SEM image in Figure 1b shows the presence of TiO2 half cap on the CoO particle, and Figure S1 shows that all of the particles have a Janus structure and their corresponding EDX. We observe that the Janus particles are not perfectly half capped due to the inherently stochastic nature of the sputtering deposition method, where the particles smaller than 2 μm in diameter have more than 50% coverage and the particles larger than 4 μm in diameter have less than 50% coverage. The contrast difference between the two layers indicates the presence of a Janus particle. It can also be seen that the CoO is faceted because of the crystallization that occurs when CoO is formed. This crystallized structure results in the formation of a porous surface, increasing the surface area of the microswimmers. We used energy-dispersive X-ray spectroscopy (EDS) in a scanning transmission electron microscope to qualitatively map the distribution of the major constituent elements of O, Ti, and Co in a CoO–TiO2 particle. The signals of Ti, Co, and O elements in Figure 1c,d also indicate the presence of a Janus structure. The XRD data of the CoO particles after annealing in Figure S2 shows the presence of only CoO and not Co3O4. The XPS data is used to conclusively prove the presence of CoO. Figures 1e and S3 show the XPS spectrum of Co 2p of CoO microparticles. The XPS spectrum of CoO shows characteristic peaks of shoulders for the main 2p3/2 and 2p1/2, indicating the presence of a pure CoO phase. DRS is used to give information on the optical band gap and absorption spectrum of the material. The slope of the DRS is used to calculate the optical band gap of the material using the Kubelka–Munk function $F(R) = (1 - R) F = (1 - R)^2/2R$, where $R$ is the reflectance. Figure 1f shows the DRS data of the CoO particles. The results show an onset absorption at 450 nm with additional absorptions from 600 nm. In this case, the optical band gap of the synthesized CoO microparticles is 2.5 eV.

EELS is a powerful tool to probe the electronic structure and response of an object in a broad spectral range, covering the ultraviolet to the infrared region, with a nanometer-spatial resolution. As seen in Figure 2a, b, the fabricated microswimmer has a broad absorption band from 0.5 to 4.0 eV, covering the spectral range of the infrared, the visible, and the ultraviolet light. Apparently, the local absorption varies from spot to spot because it is sensitive to the local environment and the interaction geometry. The peak on spectrum 1 (indicated by a red triangle) is at 3.1 eV, which is close to the rutile TiO2 band gap of 3.13 eV. Another peak on spectrum 4 (indicated by a red triangle) is at 1.78 eV, possibly corresponding to the CoO band gap of 1.76 eV.

Swimming Under Visible Light. A broad-spectrum white-light-emitting diode (LED) with an intensity of 6 mW cm$^{-2}$ is used to propel the microswimmers. The spectrum of the visible light has two major peaks at 450 and 590 nm, with no peaks in the UV region, as shown in Figure S4. Such intensity of the light used is lower than that of the other visible-light-driven swimmers in the literature, meaning that our swimmers may have higher swimming efficiency. The mean light intensity is 100 mW cm$^{-2}$, which is 17 times lower than the intensity of light used for swimming. Moreover, our microswimmers do not require any additional fuel for propulsion, where water just acts as their fuel. Figure 3a shows the mean-square-displacement (MSD) plots of their swimming trajectories under visible-light illumination. When the microswimmers are illuminated by visible light, they swim with a mean speed of 11.5 ± 0.7 μm s$^{-1}$, as shown in Figure 3b. Twenty microswimmers from different sample batches are tracked to calculate such a mean speed. It is likely that some of the microswimmers in the production batch may not be active due to the inhomogeneous temperature distribution inside the annealing chamber. When it comes to the swimming mechanisms of the microswimmers under visible light, two mechanisms can be considered. First, the microswimmers swim due to photocatalytic water splitting. The modified phase structure of TiO2 allows band bending, shown in Figure 2c, which may allow the transfer of electrons to the TiO2 conduction gap, creating an electric dipole around the particle. It is likely that the combined band gaps of CoO–TiO2 may break down water to photogenerated products at the hydrogen and oxygen evolution potentials due to the occurred redox reaction. Secondly, the microswimmers move due to self-electrophoresis mechanism due to the transfer of electrons between the two halves of the Janus structure. An ionic salt solution (1 M NaCl) is used to verify this mechanism. Under the illumination, no propulsion is observed. When the microswimmers in 0.5% H2O2 solution are illuminated, no increase in propulsion is observed, as seen in Figure S5. This may be due to the presence of NaCl inhibiting the Debye layer during the propulsion of the microswimmers. The presence of salts affects the ionic mobility on the surface of the microswimmers, leading to the ions recombining on the surface of the microswimmers.

Moreover, the swimming speed can be regulated by light intensity. The mean speed of the swimmers at the intensity of 1 mW cm$^{-2}$ is 2.07 ± 0.11 μm s$^{-1}$ at 3 mW cm$^{-2}$ is 6.2 ± 0.2 μm s$^{-1}$ and 11.5 ± 0.7 μm s$^{-1}$ at 6 mW cm$^{-2}$. The lower speed of the microswimmers can be attributed to the lower energy of the photons in the incident light. Plasmonic microswimmers like AgCl13 have shown higher speeds in the presence of blue light, but they are photocorrosive and work by breaking down to Ag$^+$ and Cl$^-$ ions under illumination, resulting in ionic contaminants, limiting their use to potential environmental applications. Other light-driven microswimmers driven by low-intensity light14,24,44.

![Figure 2](https://acsami.org/acsami/2020/12/24149/24151)

**Figure 2.** (a) High-angle annular dark-field (HAADF) imaging of a CoO–TiO2 microswimmer deposited on a thin carbon film. (b) Four zero-loss-peak-subtracted electron energy-loss spectra (EELS) acquired around the same particle as labeled in the HAADF image. (c) Band structure of the CoO–TiO2 microswimmer under visible and UV illumination.
depend on the addition of donors and redox shuttles for swimming in water. To this end, the CoO−TiO$_2$ microswimmers show the highest swimming speed at a low-intensity, full spectrum of visible light through photocatalytic water splitting without the use of redox shuttles, compared to the previous studies,$^{13,45}$ due to the better absorption of visible light, resulting in higher photocatalytic activity.

Switching the Swimming Direction under Light of Different Wavelengths. When UV light of 365 nm wavelength with an intensity of 15.5 mW cm$^{-2}$ is incident on the microswimmers, the TiO$_2$ side becomes more active as it

Figure 3. (a) Average ($N = 20$) mean-square displacement (MSD) data as a function of the time interval for the CoO−TiO$_2$ microswimmers in water under the visible and the UV light. (b) Average ($N = 20$) mean speeds of the visible-light and UV-light-driven swimmers with $p = 0.028$, the error bars represent standard error of mean. Inset photos: snapshot images of the swimmers placed in an aqueous environment at various time intervals under both visible (I, II) (Supporting Video 1) and UV (III, IV) (Supporting Video 2) light illumination. (c) Average ($N = 20$) mean speed of swimmers driven by visible light of different intensities, the error bars represent the standard error of mean. (d) Average ($N = 20$) mean speed of swimmers driven by visible light of different wavelengths, the error bars represent the standard error of mean.

Figure 4. (a) Trajectories of the wavelength control of the CoO−TiO$_2$ microswimmers under visible and UV light. (b) Snapshots of the microswimmer video (Supporting Video 3) at various time intervals with UV light (I, II) and visible light (III, IV). Scale bar: 5 μm. (c) Trajectory of the magnetically guided microswimmer under the visible light at various time intervals. Scale bar: 5 μm. (d) Vibrating sample magnetometer (VSM) data showing the magnetic properties of the microswimmer.
absorbs the UV light effectively. In this case, the propulsion is due to the light-driven self-electrophoresis, with the TiO$_2$ side becoming the driving side. The visible-light-driven and UV-light-driven microswimmers move with a mean speed of 6.5 ± 0.4 $\mu$m s$^{-1}$. The MSD and mean speed are shown in Figure 3a,b. When the UV light is incident on the microswimmer, TiO$_2$ absorbs the photons due to the energy gap of 3.2 eV resulting in a charge transfer to CoO. The mechanism of propulsion is similar to that of other TiO$_2$-based microswimmers in the literature, and their mechanism is further validated in 0.5% H$_2$O$_2$ solution. These microswimmers show increased propulsion, indicating that TiO$_2$ breaks H$_2$O$_2$ under the UV light, as shown in Figure S5. The change in the active cap side makes the microswimmers move in a direction opposite to the direction they move under the visible light illumination.

The visible light used for the propulsion of the swimmers has a broad spectrum, ranging from 400 to 700 nm. To measure the dependence of CoO–TiO$_2$ swimmers on the wavelength of illumination, visible light of three wavelengths of 455, 511, and 605 nm at 20 mW cm$^{-2}$ intensity are selected. The mean speeds of the swimmers at different wavelengths are shown in Figure 3d. The fastest swimming speed is 7.1 ± 0.3 $\mu$m s$^{-1}$ at 455 nm and the slowest is 5.5 ± 0.3 $\mu$m s$^{-1}$ at 511 nm. This is due to the presence of an absorption peak of CoO around 450 nm, while the absorption is the lowest at 511 nm, resulting in a lower speed.

The mean speed of the swimmers in individual wavelengths is still two times lower than the mean speed under visible light, indicating that our swimmers absorb a plethora of wavelengths, enabling better charge separations and thus faster mean speeds.

**Guiding the CoO–TiO$_2$ Microswimmers.** A thin film of magnetic materials, such as Co or Ni, has been predominantly applied to steer the microswimmers. Additional magnetic layer, however, may lower the speed of swimming, which hampers the electron transfer between different layers of the Janus structure and thus obstructs the charge separation. In the case of CoO–TiO$_2$ microswimmers, there is no need for an additional magnetic film coating. This unique characteristic of the microswimmers comes from the inherent magnetic properties of CoO. CoO is known to be antiferromagnetic, though its Neel temperature is only 298 K, above which they are paramagnetic. Due to the oxygen deficiency created during the annealing process, some Co is formed in the crystal lattice of CoO. Co is ferromagnetic in nature and provides the magnetic property, which can improve the performance of the microswimmers. This property of the CoO–TiO$_2$ microswimmers can be characterized by vibrating sample magnetometer (VSM) measurements. The hysteresis curves shown in Figure 4d indicate the presence of Co on the swimmers, making them ferromagnetic in nature. They can also be steered using relatively low-strength magnetic fields (~8 mT) applied by an external permanent magnet. The direction of the microswimmers can be controlled by changing the direction of the applied external magnetic field. Figure 4b shows the trajectory of the microswimmers under the applied magnetic field.

Controlling the swimming direction without the use of phototaxis enables additional degrees of freedom for the control of light-driven microswimmers. Thus, the CoO–TiO$_2$ microswimmers have the unique ability that the direction of their propulsion can be changed by illuminating visible or UV light on them. The use of light at different wavelengths enables the activation of different layers of the microswimmers, causing the microswimmers to change their swimming direction depending on the symmetry of the Janus structure. However, they are inherently asymmetrical during the fabrication process and crystallization, resulting in an imperfect Janus structure. In Figure 4a, the trajectories of five different CoO–TiO$_2$ microswimmers from different batches are monitored to confirm the symmetry effect. The microswimmers are first illuminated with visible light and then successively illuminated with UV light. Under visible-light illumination, they form the driving side. The CoO being larger in volume within the swimmers, combined with larger sizes of the swimmers, causes them to move in a straight trajectory without much rotation or tumbling, as seen in the trajectories of the microswimmers. When the swimmers are only illuminated with UV light, the TiO$_2$ side acts as the driving side and the CoO side is passive, leading to a change in the swimming direction. Under UV illumination, there is a change in the electron field direction around the swimmers, with the electrons now moving from the CoO to the TiO$_2$ side, resulting in the direction change for the microswimmers. Multiple cycles of successive light switching between visible and UV wavelengths result in a change in the direction each time (Figure S6). Hence, the direction of swimming can be reversed when the type of illumination is changed, which is potentially controlled by regulating the wavelength of light. This wavelength-dependent direction change enables another mode of control for light-driven microswimmers, which, to the best of our knowledge, has not been explored in the literature yet. This wavelength-based steering combined with their ability to load drugs and cargos would in the porous structure of the swimmer body enable potential applications of visible-light-driven swimmers in future in vivo cargo delivery applications.

**CONCLUSIONS**

Here, we have developed a fabrication methodology for creating multiwavelength-responsive CoO–TiO$_2$ microswimmers propelled by low-intensity, UV-free, visible-light illumination. The microswimmers show enhanced swimming speeds under both visible and UV light illumination and are multiwavelength controllable, enabling direction change of the microswimmers by changing the wavelength of the light. The microswimmers are active under both visible and UV light due to the unique combination of materials, allowing for selective absorption on both sides of the Janus structure, causing the swimmers to change their swimming direction. Moreover, they can be precisely steered by an external magnetic field direction since CoO is magnetic. Such microswimmers have potential applications in target drug delivery, active photocatalysis, and hydrogen evolution.

**MATERIALS AND METHODS**

CoO$_2$ microparticles were purchased from Sigma-Aldrich. Images of CoO–TiO$_2$ Janus structure of the microswimmers were imaged by a Zeiss ULTRA 55 SEM. Scanning transmission electron microscopy-based electron energy-loss spectroscopy (STEM-EELS) measurements were performed with a subelectron-volt sub-angstomicroscope (SESAM, Zeiss, Oberkochen, Germany) at an acceleration voltage of 200 kV. The full convergence and collection angles were 14 and 13 mrad, respectively. The acquisition time for each EEL spectrum was 1.5 s. EDX spectrum imaging was conducted with a Thermo Scientific NORAN EDX system. A Carry 5000 ultraviolet–visible (UV–vis)–NIR spectrometer with an integrating sphere is used for DRS. A Thorlabs M36SL2 (Germany) UV lamp with 365 nm wavelength and 15.5 mW cm$^{-2}$ intensity is used for illumination through a Zeiss Axios A1 inverted microscope. The videos are recorded from the microscope using a LD Plan-NeoFluar 40x objective lens and an Axiocam 503 charge-coupled device (CCD) camera at 62 fps. The swimming
behavior of the swimmers is systematically investigated by two-dimensional MSD swimming analysis on the captured videos using a custom MATLAB code.

**Microswimmer Fabrication.** Co$_3$O$_4$ microparticles had a size distribution of 2–6 μm. These microparticles were spherical in shape. Co$_3$O$_4$ microparticles were deposited on a silicon wafer by drop-casting. A 40 nm thick TiO$_2$ layer was sputtered on them. These Janus Co$_3$O$_4$–TiO$_2$ particles were then annealed in an Ar atmosphere at 1000 °C in systematic annealing to reduce Co$_3$O$_4$ to CoO.$^{27}$ Initially, the temperature was ramped up to 800 °C in 30 min and further heated to 1000 °C in 2 h. The temperature was then held at 1000 °C for 10 h. This dwelling time allowed for a stable CoO crystal structure. The annealing process helped in crystallizing the CoO microstructure. The Ar atmosphere allowed the oxygen from the cobalt to diffuse, resulting in the reduction of Co$_3$O$_4$ to CoO.$^{27}$ This process also crystallized TiO$_2$ to its rutile phase. Ar gas was circulated at 25 sccm throughout the annealing process. It was then subsequently cooled down to 900 °C within 30 min and then to room temperature within 10 h. The slow cooling was essential to maintain the crystal structure and prevent the reoxidation of CoO. It also made them photoactive. The annealing process made the microswimmers reactive to the visible light. A reduction in size occurred due to annealing, resulting in a smaller size dispersion of 1–4 μm. The particles were then sonicated and removed from the surface. These microswimmers were then used for characterization and swimming. We produced thousands of particles in each run. There was batch-to-batch variation due to the variation of particle coverage during drop-casting of the CoO particles.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c06100.

- EDX, XRD, spectrum of light, and mean speed data in H$_2$O$_2$ (PDF)
- Visible light (MP4)
- UV light (MP4)
- Wavelength control (MP4)

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**Author Contributions**

V.S., B.-W.P., and M.S. conceived and designed the research. V.S. designed and performed the experiments, analyzed the experimental data, and drafted the manuscript. M.S. and B.-W.P. contributed to the discussions and edited the manuscript. S.S. and P.A.v.A. provided the results for the TEM and EELS characterization.

**Notes**

The authors declare no competing financial interest.

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