Photocatalytic BiVO₄ Microswimmers with Bimodal Swimming Strategies

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Photocatalytic micromotors are developing rapidly and environmental applications seem very promising and within reach. However, the complex synthesis strategies, jointly with the large band gaps of most efficient swimmers inhibit both, applications and upscaling. Herein, a simple solvothermal synthesis of well defined, catalytically active BiVO₄ microparticles, which can propel efficiently without asymmetrization is presented. Those microparticles respond to blue and UV light and are able to switch between different motion strategies, similar to bacterial microswimmers. These behavioral changes are controlled by changing the pH value of the environment.

1. Introduction

Biological swimmers like bacteria are able to adapt their swimming modes to the circumstances to maximize their swimming efficiency, and therefore, the chance to find nutrients. In their study, Hintche et al. investigated Pseudomonas putida in the vicinity of solid surfaces and found a dominating pusher type behavior with a slight bending, which can be associated to hydrodynamic coupling with the wall.[1] However, the authors found that these lophotrichous bacteria can also switch to a counterclockwise rotation of their flagella and thereby to pulling motion. A third swimming strategy is accessible: wrapping the flagellar bundle around their body and move in a corkscrew manner. Different from the other two, this motility mode results in mostly straight paths, which is supposed to be used not only in more viscous environments but also seems to facilitate escape from narrow surroundings.[2]

For artificial micromotors, such smart adaptive behavior has yet to be reported. Controllable swimming modes for catalytic Janus particles were developed by Archer et al. Their findings show that the tendency to rotate could be permanently tuned using a nonuniform catalytic patch which modifies the torque on the motion and can easily be obtained through differently packed monolayers of colloids in glancing angle deposition.[3] Later, Bechinger and co-workers published a surface-based strategy to straighten the paths of L-shaped swimmers in critical mixtures.[4] Shelke et al. discovered that catalytic microswimmers with different geometric shapes can swim in different orientations, depending on the fuel concentration. These particles were synthesized using a liquid–liquid interface approach. Swollen polystyrene particles undergo a shape change as they were heated above their glass transition temperature and were subsequently covered by Pt at a glancing angle.[5] Therefore, the bottom heavy particles can be oriented with the flat side toward the glass or move at a sliding angle. It was found that the motility mode depends on fuel concentration. At low concentrations (0.5–1%), self-propulsion and Brownian fluctuations compete, and the particles undergo self-propelling, almost linear motion, whereas at higher concentrations (2–5%), the authors found two different random swimming orientations: when the particles were lying on the substrate, the motion was rather linear, whereas an upright orientation led to mostly circular motion.[6] However, here the orientation of the motors was neither controllable nor directly connected to external circumstances. Interesting findings on different geometries that indicate further hydrodynamic constraints were made by Baker et al.[7] In general, the orientation of catalytic micromotors was found to be strongly dependent on the presence of surfaces due to the general density mismatch that forces most microswimmers in the close vicinity to the substrates.[8]

Uspal et al. predicted sliding states for Janus particles suspended in a Newtonian solution close to a chemically inert and impenetrable planar wall. Assuming that the catalytic cap releases a solute, there are possible agents causing the change of orientation respectively to the wall: 1) wall-induced changes in the solute gradients, coupling back to the phoretic slip on the particle surface or 2) confinement of the hydrodynamic flows, or 3) different surface mobilities cause nonuniform product repulsion from the two sides. They concluded from numerical simulations that for uniform particles, the hydrodynamics dominate the turning behaviors, except for positions very close to the wall. In addition, different surface mobilities can cause a wall-induced chemical gradient to drive a rotation respective to the wall, obtaining sliding and hovering states. Later, they refined the model and achieved a 0° orientation according to experimental findings,[9] isolated and quantified the different wall-induced contributions to particle motion.

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DOI: 10.1002/aisy.201900093
However, as of today, all microswimmers that showed defined orientations required complex sample preparation steps. On the other side, thinking about potential future applications and upscaling, “non-complicated” production strategies are required, for which deposition-based techniques are not ideal.

Here, we use a one-step solvothermal fabrication method that does not require further material processing to produce overall symmetric swimmers that possess enough inherent asymmetric restrictions to undergo active motion. Depending on the pH conditions, these smart particles can switch between two motion modes.

2. Results and Discussion

2.1. Material Synthesis

It is generally known that microswimmers require a constant energy input for their movement at low Reynolds numbers, as viscous forces in that regime outrule inertia.[10] For photochemically propelled swimmers, this energy input is provided by the localized degradation of chemical fuels. Different semiconducting materials have been suggested to fulfill this requirement. Depending on their band gap, they can be excited with light of the corresponding wavelength. Many systems have been studied, most of them relying on TiO₂ as the photochemically active material.[11]

Bismuth vanadate (BiVO₄) is one of the most promising photoelectrocatalysts due to its band gap of 2.3–2.5 eV, which corresponds to the visible region. In addition, its large absorbance rate sets good preconditions for high efficiencies.[12] Unfortunately, a low band gap alone will not necessarily lead to an efficient photocatalyst. Other key factors, like the recombination rate, surface area, and charge of the material, play an important role in photochemical efficiency. Depending on the conditions and the composition of the synthesis, different morphologies of BiVO₄ have been obtained. Examples are spheres, fishbone-like structures (Figure S1, Supporting Information) and stars.[13] To these different geometries and associated crystal facets, different activities have been assigned. Especially for the monoclinic crystal structure, characteristic BiVO₄ nanoplates with exposed [010] facets (corresponding to the [040] reflex in the XRD) have been found and their photocatalytic activities have been analyzed in detail.[14]

In this work, we introduce a new morphology of square-shaped, layered BiVO₄ microparticles, which show excellent photochemical activity in UV and also visible light in the blue range (Video S1, Supporting Information and Table 1).

Remarkably, when immersed in H₂O₂, these particles perform active propulsion. However, as their shape is overall symmetric, this behavior imposes the general question, where the motion originates from. To answer this question, we propose two hypotheses: First, the motion could be explained by environmental fluctuations, which lead to initial asymmetric gradients followed by a ballistic motion of the particles. Second, although not overall asymmetric in shape, inherent anisotropic stackings of the crystal facets can lead to geometric constraints on the gradient formation or, expressed differently, the side stacks of the BiVO₄ crystals present very rough morphologies, which could account for asymmetry. To decide between the two, we designed further experiments. We investigated the behavior of high and low particle densities and analyzed individual particle orientation in consecutive activation cycles. To understand the influence of environmental conditions, we studied the influence of the solution pH.

The particles were synthesized by a solvothermal approach in a water/ethanol/ethylene glycol solvent mixture. Characterization was conducted by scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and powder X-ray diffraction (XRD). The results reveal a square-shaped morphology with low polydispersity of 2.0 ± 0.2 μm in size (Figure 1B). BiVO₄ commonly appears in two different crystal structures, monoclinic scheelite and tetragonal zircon.[15] As the monoclinic structure has a lower band gap than the tetragonal one, it is enabled to catalyze photochemical reactions under visible light.[16] From the XRD data, it can be concluded that these particles mainly consist of the monoclinic structure, with a small amount of tetragonal zircon phase (Figure 1C). This is also further confirmed by DRS measurements, which reveal visible absorption of the particles (Figure 1D).

The particle surface charge and especially the point of zero charge (PZC) strongly influence which substances are adsorbed to the catalytic surface, and therefore, also how the photochemical reaction proceeds. As the degradation of the fuel and the created product gradient substantially influence the driving force of the microswimmer motion, variation of the surface charge has been used here to achieve different propulsion modes. By adjusting the dispersant pH, the particle surface charge can be influenced. In Figure 2, the zeta potential of the particles depending on the solution pH is shown. The PZC of BiVO₄ can be determined to pH = 3.4 and is in good agreement with theoretical and experimental results of other research groups.[16,17] Below the PZC, H₂O₂ ions adsorbed to the crystal surface lead to an overall positive charge of the particles. At pH = 3 and pH = 2.5, the particles show a horizontal sliding motion, whereas at pH = 2, we observe a strong tendency to stick to the surface (see Video S2, Supporting Information). This can be explained by the increased ionic strength caused by the added protons and Cl⁻ ions, which is also displayed by increasing conductivity values for decreasing pH. These ions directly influence the adsorption properties of the particles as they minimize electrostatic repulsion between particles and the substrate.

Above the PZC, negatively charged OH⁻ ions cause a negative surface charge of the particles. At pH = 4 the surface

| pH | Zeta potential [mV] | Movement mode | Light source | Speed [μm s⁻¹] |
|----|---------------------|---------------|--------------|----------------|
| 7  | -49.4 ± 1.65        | Upright sliding | UV           | 6.13 ± 0.86    |
| 3  | 4.17 ± 1.36         | Horizontal sliding | Blue         | 2.14 ± 1.04    |
charge is only slightly negative and the electrostatic repulsion of the surfaces (both, negative and positively functionalized glass slides have been tested) is not large enough to overcome gravity and particles frequently stick to the substrate. For all analyzed conditions at pH values between 5 and 9, an upright sliding motion is observed (see Video S3, Supporting Information).

2.2. Movement Modes

As briefly introduced previously, we observe two movement modes under different conditions. Whereas negatively charged particles move on their side face, positively charged ones slide on their ground face. See Table 1 for a summary of the properties in different conditions. Despite having distinct speeds within the same order of magnitude for both modes, their orientation in influences interaction with the substrate as well as the hydrodynamic exposure area significantly. A detailed study of these modes and their pH dependence is presented in the following.

To investigate the upright sliding performed by negatively charged BiVO₄ particles, pH = 7 was chosen as an example condition, as it provides the most favorable environment for catalytic micromotors due to its lowest ionic strength. The particles were dispersed in deionized water with a H₂O₂ content of 0.1%. At these conditions, the ion content of the sample solution is minimal, which favors the electrostatic repulsion between the negatively charged surfaces of the BiVO₄ with a zeta potential of $-49.4 \text{ mV}$ and the glass slide, which prevents particle sticking.

Upon irradiation with UV light, the particles laying on their ground face rotate vertically by 90° and then perform an upright motion on their side face (Figure 3 and Video S3, Supporting Information) at average speed of $6.13 \pm 0.86 \text{ μm s}^{-1}$, up to $6.98 \text{ μm s}^{-1}$. When irradiated with blue light, the same
motion pattern is observed at decreased average speed of $3.83 \pm 0.46 \, \mu \text{m s}^{-1}$. This behavior seems to be rather consistent over flat BiVO$_4$ particle morphologies, as it is partially similar to observations by Villa et al.\cite{13} The particles often present curved trajectories, however, also straight lines, similar to the findings of Ma et al., are possible as shown in Figure S2, Supporting Information.\cite{18}

The motion pattern is particularly remarkable as these particles have not been modified to turn them into asymmetric Janus particles for which this 90° rotation upon activation of the system has been studied previously by Simmchen et al.\cite{9}

By carefully looking at the activation of several particles with UV light, we observe that the upright rotation happens immediately upon irradiation and simultaneously for all particles. Therefore, environmental fluctuations, such as the vicinity of other particles, are not likely to cause the motion pattern, as they would lead to significantly different stand-up behavior for each particle. In addition, for such large particles, the expected influence of environmental fluctuations is rather small.

In consequence, the source of motion is likely to be an inherent particle property, like anisotropic stacking of crystal facets. It has been shown before that different crystal facets of BiVO$_4$ show different photochemical reactivities.\cite{16,19,20} In addition, Li et al. showed that the excited electron-hole pair undergoes spatial separation among [010] and [110] facets of a BiVO$_4$ single crystal.\cite{21} Zhao et al. found preferentially exposed [010] facets in shuriken-like morphologies of BiVO$_4$ microparticles\cite{22} and an accumulation of holes in the [110] was detected by Zhu et al.\cite{23} For this reason, we assume that the side faces of the here-synthesized particles correspond to stacks of [110] facets, the holes should preferentially accumulate there, and consequently, we assume the sides as the location of peroxide reduction. This means, while the particles appear symmetric when investigated with electron microscopy, it is possible that the stacking of the different [110] crystal facets is anisotropic.

In line with the findings of Zhao et al. and Zhu et al., we suppose a similar photochemical activity on the ground and top face of the particles, which the XRD in Figure 1C suggests to be [010] facets. This leads to their upright rotation away from the substrate, most likely caused by the peroxide oxidation products. We suppose a significantly different activity among the four side faces, so that a preferential upright position and motion direction is caused by the aforementioned stacking anisotropy. To probe this hypothesis, we investigated the motion pattern of several particles, whereas undergoing three consecutive illumination cycles (Video S4, Supporting Information). We find that seven out of eight fully trackable particles in one video rotate up to the same of the four side faces and undergo motion in the same direction in each illumination cycle. Figure 4 illustrates this behavior for an example particle (see also Video S5, Supporting Information). The purple arrow in Figure 4 marks the same side face of the particle at different time points. Upon UV irradiation, this side face points to the top in each excitation cycle. It can be seen that even the vicinity of other particles does not influence the 3D orientation upon irradiation.

This behavior can also be found when single particles are investigated. Therefore, geometric constraints are assumed to be the source of the motion pattern of these particles.

However, as particle reactivity not only depends on intrinsic material properties exclusively, but also on environmental factors, we investigated the particle motion at pH values between 2 and 3, where the zeta potential of BiVO$_4$ is found to be positive.

To reduce the pH to 3, the particles were dispersed in $1 \times 10^{-3}$ M hydrochloric acid. Reducing the solution pH, H$_3$O$^+$ ions are adsorbed to the BiVO$_4$ surface, which accounts for a slightly positive zeta potential of 4.17 mV. To observe particle motion and overcome electrostatic attraction, glass slides modified with (3-aminopropyl)triethoxysilane were prepared, which leads to a positive surface charge of the substrate. We exemplify pH = 3 for further investigation of the motion pattern of positively charged particles. At these conditions, the particles show no vertical rotation upon irradiation, but perform horizontal sliding motion on the glass surface (see Figure 5 and Video S2, Supporting Information). We observe lower particle speeds with a maximum at $4.52 \, \mu \text{m s}^{-1}$ and an average of $3.78 \pm 0.60 \, \mu \text{m s}^{-1}$, for which the higher ion content of the sample or a decreased photochemical activity can be the reason. Similar to negatively charged particles, blue light illumination also leads to a decrease in average particle speed to $2.14 \pm 1.04 \, \mu \text{m s}^{-1}$. Due to the slightly concave side faces, this motion mode could potentially be used for selective cargo transport, as shown in Figure S3, Supporting Information.

Figure 3. A) Mean square displacement (MSD) of a BiVO$_4$ particle at pH = 7, 0.1% H$_2$O$_2$, and 50% UV illumination. B) Snapshots of the corresponding particle track. Upon UV illumination, the particle rotates vertically by an angle of 90° and starts moving. Scale bar is 2 µm.
As the crystal structure is not affected by changing the solution pH, the absence of a 90° rotation of the particles upon activation of the system with UV light indicates a change in the photochemical reaction mechanism. As the surface charge of BiVO₄ is inverted, the adsorption capability of H₂O₂ fuel and reaction intermediates is affected, which can influence the motion pattern and speed. It can be assumed here that either the decreased photochemical activity of positively charged BiVO₄ surfaces or the high ion content decreases the propulsion efficiency and leads to the absence of upright rotation.

3. Conclusions

In conclusion, we present a one-step synthesis for highly active, photochemically driven BiVO₄ microswimmers with a unique square-shaped, layered structure. Although not asymmetric in shape, these particles allow us to switch between upright and horizontal sliding motion under UV and visible light irradiation at speeds up to 6.98 μm s⁻¹, depending on the solution pH and the zeta potential of the particles. Investigation of consecutive illumination cycles showed that the particle orientation is consistent over each activation, which leads to the conclusion that asymmetric constraints of the crystal facet orientation in the particles give rise to motion. These particles have a high potential for production scale-up, as they do not require further modification steps to introduce asymmetry after the synthesis. Concurrently, these simple particles modify their swimming strategy depending on external conditions. This enables them to maneuver through complex environments, similarly to the motion pattern of _P. putida_. Adaptable navigation through complex environments is a key feature for microswimmers to solve elaborate tasks.

4. Experimental Section

**Syntheses—Synthesis of Bismuth Vanadate Microsquares:** In an 100 mL Erlenmeyer flask, concentrated nitric acid (2.5 mL) was added to a 1:1 mixture of ethanol and ethylene glycol (12.5 mL). Next, dodecylamine (2.78 g, 15 mmol) was added and dissolved under stirring. Afterward, Bi(NO₃)₃ (2.425 g, 10 mmol) and NH₄VO₃ (0.585 g, 10 mmol) were added under stirring. After dissolution, the pH was adjusted to 3 with a 2 M...
NaOH solution (in H2O:ethanol:ethylene glycol in a 0.5:1:1 ratio), and a brownish precipitate was formed. The solution was transferred to a 50 mL Teflon-lined autoclave and left to ripen for 3 h, which was then followed by a heat treatment at 100 °C for 12 h. The particles were then carefully washed three times with ethanol and dried at 60 °C for 12 h.

**Syntheses**—**Glass Slide Functionalization**: Cover glass slides with dimensions 20 mm × 20 mm were cleaned by immersion in concentrated hydrochloric acid for 30 min. After extensive washing with deionized water, slides were cleaned with acetone and ethanol for 5 min each under ultrasonication. After drying with pressured air, the slides were plasma cleaned for 5 min in an oxygen plasma. For experiments at pH = 5–9, the slides were used without further cleaning. For experiments at pH = 2–3, a functionalization with (3-aminopropyl)triethoxysilane (APTES) by evaporation was conducted. Two slides each were prepared in a single use Petri dish with APTES (70 µL) and then transferred to a desiccator, where they were kept under reduced pressure for 3 days.

**Characterization**—**Powder X-ray Diffraction**: XRD patterns were acquired using a Bruker 2D phaser in a 2θ range of 10°–100°, where symmetrical scans were performed. The microparticles were dispersed in ethanol and drop casted on a Si wafer.

**Characterization**—**Scanning Electron Microscopy**: For SEM imaging, diluted solutions of BiVO4 microparticles were drop casted on aluminum tape-coated sample holders and dried overnight. The images were obtained using a Zeiss DSM 982 GEMINI electron microscope.

**Characterization**—**Diffuse Reflectance Spectroscopy**: DR measurements were recorded in diluted aqueous particle solutions using a Cary 60 spectrophotometer (Agilent Technologies).

**Characterization**—**Microscope Experiments**: For experiments at different pH, aqueous solutions at pH values between 2 and 9 were prepared from concentrated hydrochloric acid and sodium hydroxide pellets in 50 mL measuring flasks. For the experiment, a few milligram of BiVO4 particles were dispersed in 1 mL aqueous solution of a certain pH by ultrasonification for 3 min. Then, 9 µL of the solution was mixed with 1 µL 1% H2O2 and the particle motion was observed in the microscope. Sample illumination was performed with a flexible Colibri light source of 385 and 469 nm for UV and blue excitation, respectively. Experiments were usually done under 50% illumination intensity, where 100% corresponds to 315 mW for UV and 230 mW for blue light.

**Characterization**—**Zeta Potential Measurements**: Zeta potential was measured with a Malvern Zetasizer Nano ZSP in autotitration mode. A diluted particle dispersion was adjusted to pH = 10 with sodium hydroxide solution and titrated in 0.5 pH steps with 0.01M hydrochloric acid at pH values between 4 and 9.5 and with 0.1M hydrochloric acid at pH values between 1.5 and 3.

**Characterization**—**Video Evaluation/Tracking**: Video analysis was performed with ImageJ 1.52e software and videos were tracked with the TrackMate plugin[24] and resulting track files were processed with MATLAB R2018b.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors thank the Volkswagen foundation for the Freigeist fellowship (grant number 91619), as well as the Kaercher foundation for financial support.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

BiVO4, micromotions, pH dependence, smart switching, symmetric swimmers

Received: July 31, 2019
Revised: August 22, 2019
Published online: October 3, 2019

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