Better fuels for photocatalytic micromotors: a case study of triethanolamine†

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Efficient fuels are critical for designing photocatalytic micromotors with high performance. We discover that 0.5 mM of triethanolamine can power TiO₂–Pt motors at 35 μm s⁻¹ without producing bubbles, a significant improvement over conventional fuels such as water, H₂O₂ or hydroquinone. The effectiveness of hole scavengers such as triethanolamine can be generalized to other photocatalytic micromotors containing a heterojunction with an n-type (but not a p-type) semiconductor.

Inspired by biological motors, synthetic micro- and nanomotors convert the energy stored in their environment into mechanical work, and as a result, move autonomously in fluids.¹⁻⁵ In particular, motors powered by surface photocatalysis (known as "photocatalytic micromotors")⁴⁻⁵ are easy to handle and be controlled remotely, and are potentially useful in the degradation of microplastics and other organic pollutants.⁶⁻⁷ However, they often suffer from low energy conversion efficiency,⁸ and therefore require a high level of light intensity and fuel concentration to operate, which in turn greatly limits their usefulness in realistic scenarios.

In light of these challenges, there have been continuous efforts in designing photocatalytic micromotors that move faster and consume less fuel. One direction is to design micro- and nanomotors with better semiconductor materials⁹⁻¹⁰ or via optimizing motor structures¹¹⁻¹² but this often involves complicated sample fabrication or materials. The second direction is to use fuels beyond water, such as H₂O₂,¹³⁻¹⁴ hydroquinone/benzoquinone (H₂Q/BQ),¹⁵⁻¹⁶ hydrazine,¹⁷ glucose,¹⁸ and urea.¹⁹ There is a continuous need to discover new fuels that are of high performance.

In this communication, we report a new fuel, triethanolamine ("TEOA"), that powers a typical photocatalytic micromotor (TiO₂–Pt) at a speed that is 5 times that in pure water, 4 times that in H₂O₂, and 3 times that in hydroquinone (see Video S1, ESI†). Additional key advantages of TEOA include a low operating concentration, a low requirement on light intensity, mild salt tolerance, and lack of bubbles. TEOA is an effective fuel because it serves as a hole scavenger that significantly boosts the kinetics of the photoanodic half-reaction of a TiO₂–Pt micromotor,²⁰ a design principle that can be generically applied to other photocatalytic micromotors.

Throughout this communication, a TiO₂–Pt Janus microsphere is used as a model for a photocatalytic micromotor, which has been a popular subject of study over the years.²¹⁻²⁴ These Janus microspheres are fabricated by half-coating titanium dioxide (TiO₂) microspheres (1.2 ± 0.1 μm in diameter) with a layer of platinum (Pt) (Fig. 1a, see ESI† for synthesis details). Under UV light irradiation, TiO₂ generates electrons and holes that react at the surface of Pt and TiO₂, respectively (see Fig. 1b for a schematic). They then react with fuel molecules and create a self-generated electric field that propels a...
micromotor away from the Pt end. This mechanism, known as self-electrophoresis,\textsuperscript{24–26} has successfully explained the self-propulsion of photocatalytic micromotors with a metal-semiconductor heterojunction.\textsuperscript{27,28}

A key component in this mechanism is the choice of fuel molecules. Popular choices include water, \( \text{H}_2\text{O} \), and the benzoquinone (BQ)/hydroquinone (\( \text{H}_2\text{Q} \)) pair. TEOA compares favourably to all these fuel molecules in several aspects. The most prominent advantage of TEOA is its effectiveness in powering motors at high speeds. For example, as shown in Fig. 1c, the trajectories of a TiO\(_2\)-Pt micromotor are noticeably longer in 0.5 mM of TEOA than those in water, 100 mM H\(_2\)O\(_2\), or 50 mM H\(_2\)Q (the optimal concentrations determined for each fuel, see Fig. S2, ESI\textsuperscript{†}). Correspondingly, the motor speeds are highest in 0.5 mM TEOA, reaching 35 \( \mu \text{m s}^{-1} \) (30 body lengths per second).

Note that speeds on the order of tens of body lengths per second have been reported for TiO\(_2\)-based photocatalytic micromotors.\textsuperscript{21,24,27,29,30} However, it is generally challenging to compare absolute speeds across different literature reports, because of possible differences in material preparation and operating conditions. As a result, speeds of TiO\(_2\)-Pt micromotors in TEOA in this communication are compared with those in H\(_2\)Q and H\(_2\)Q from our own labs under the same lighting conditions. Moreover, the speeds of TEOA-powered motors can potentially be further improved by optimizing their material properties\textsuperscript{31,32} or coating composition.\textsuperscript{33}

In addition to fast speeds, other advantages of TEOA as a fuel molecule are further quantified in Fig. 2. First, Fig. 2a shows that a TiO\(_2\)-Pt motor can self-propel in TEOA of a wide range of concentrations (\(10^{-2}\) to \(10^2\) mM), reaching a peak speed at 0.5 mM of TEOA. Motor speeds decrease at higher concentrations possibly because TEOA as an organic base readily reacts with water and form ions, which are known to slow down self-electrophoretic motors.\textsuperscript{34–36} Note that the concentration of TEOA can be as small as 0.01 mM, which is orders of magnitude smaller than typical fuels used in the literature (e.g., H\(_2\)O\(_2\) and hydrazine),\textsuperscript{17} and of negligible toxicity to cells.\textsuperscript{37}

Second, Fig. 2b shows that the speeds of motors in TEOA and water both monotonically increase as light intensity increases, but the motor speed at lower light intensities (123 mW cm\(^{-2}\)) in TEOA is comparable with that at high light intensities (650 mW cm\(^{-2}\)) in water, a useful feature if low lighting is preferred (for example to minimize photobleaching of dyes). Third, similar to other fuels, motors in TEOA slow down significantly during prolonged light irradiation (Fig. 2c),\textsuperscript{38} possibly because of the deactivation of the catalyst surface over time. However, motors in TEOA after 10 minutes still move twice as fast as those in water, a feature useful for studying their collective behaviours over a long time. Furthermore, no bubble was produced even after tens of minutes of operation or with a large motor population. This is because, instead of producing O\(_2\), holes react with TEOA to yield TEOA\(^-\).\textsuperscript{39} Finally, Fig. 2d shows that the boosted performance of TEOA enables the propulsion of a TiO\(_2\)-Pt motor in ionic strength of 5 mM, whereas water-powered micromotors show Brownian motion in the same ionic strength.

The most common way for a fuel molecule to improve the performance of a photocatalytic micromotor is by accelerating the reaction and thereby increasing the photocurrent. In the particular case of TiO\(_2\)-Pt, the Pt cap not only promotes the separation of photogenerated electrons and holes, but also acts as a co-catalyst that facilitates the reaction of electrons on its surface.\textsuperscript{40,41} TiO\(_2\), on the other hand, is known to be a mediocre cocatalyst for oxygen evolution, and thus the consumption of photogenerated holes on the surface of TiO\(_2\) becomes the rate-limiting step.\textsuperscript{42,43} Therefore, to expedite this half-reaction, and thereby increasing the overall photocurrent, hole scavengers such as H\(_2\)Q,\textsuperscript{44} H\(_2\)O\(_2\),\textsuperscript{45} and alcohols\textsuperscript{46} are commonly used as fuels in photocatalytic micromotors. The same principle also applies to TEOA, which is known to be a good hole scavenger in the literature of photocatalytic hydrogen production.\textsuperscript{47–49}

To confirm that the effectiveness of TEOA indeed stems from an increase of the photocurrent, we measured the photocurrent between a TiO\(_2\) film and a Pt film with a typical three-electrode electrochemical cell (Fig. 3a, see ESI\textsuperscript{†} for experiment details and Fig. S3 for more results). In all measurements we report below, photocurrents flow from Pt (cathode) to TiO\(_2\) (anode), consistent with the self-electrophoresis mechanism depicted in Fig. 1d. Importantly, under UV irradiation of 650 mW cm\(^{-2}\), we recorded a photocurrent of 2.7 mA cm\(^{-2}\) in 0.5 mM of TEOA, much larger than that acquired in 100 mM H\(_2\)O\(_2\) (0.65 mA cm\(^{-2}\)) or 50 mM H\(_2\)Q (0.79 mA cm\(^{-2}\)). This comparison in photocurrent (Fig. 3b) also agrees nicely with that of motor speeds among different fuels, and is thus a powerful indication that the effectiveness of TEOA lies in an improvement in the reaction rate of photocatalysis on TiO\(_2\)-Pt.

**Fig. 2** Water- or TEOA-powered TiO\(_2\)-Pt micromotors under different experimental conditions. (a and b) Influence of TEOA concentrations (a) and UV light intensity (b) on motor speeds. (c) Speed of motors under continuous illumination over time. (d) The effect of adding salt (final concentration 5 mM NaCl) to TiO\(_2\)-Pt motors powered by water or 0.5 mM of TEOA. In all figures, data in pure water are coloured grey, and those in TEOA are green. Error bars represent standard errors from 20 independent measurements.
TiO$_2$ is unlikely, given that the fundamental material properties (i.e. a better separation of photoelectrons and holes), thermodynamics (i.e. TEOA reacts more easily with holes), or kinetics (i.e. TEOA consumes holes faster). The first possibility of TEOA generating more electrons and holes out of TiO$_2$ is unlikely, given that the fundamental material properties and light absorption of TiO$_2$ remain unchanged. Second, the electrochemical potential of TEOA$^+$/TEOA (0.82 V vs. NHE), is larger than that of O$_2$/H$_2$O$_2$ (0.69 V) or BQ/H$_2$Q (0.70 V), suggesting that thermodynamically TEOA is in fact a worse hole scavenger than H$_2$O$_2$ or H$_2$Q.

This leaves it the only possibility that TEOA improves the kinetics of the photocatalytic reaction on TiO$_2$–Pt. This is reasonable, because an early study shows that the oxidation of TEOA by photogenerated holes is preceded by a deprotonation process, which is a fast kinetic process that reduces the energy barrier in the electron transfer process.$^{34}$

$$\text{TEOA} \rightarrow \text{TEOA}^+ \rightarrow \text{HOCH}_{2}\text{CH}_2\text{NCH}_2\text{CHO} \ (1-1)$$

Finally, we extend the observed improvement in speeds of TiO$_2$–Pt micromotors by TEOA to other photocatalytic micromotors. In Fig. 4a and b and Video S3 (ESI†), we show that both a TiO$_2$–Au micromotor made of coating gold (Au) instead of Pt on TiO$_2$ microspheres, and a ZnO–Pt micromotor made of coating Pt on zinc oxide (ZnO, also an n-type semiconductor) microspheres, show a significant boost in speeds when TEOA is present. TEOA is effective in these two cases because TiO$_2$–Au and ZnO–Pt, like TiO$_2$–Pt, contain heterojunctions between an n-type semiconductor and a metal of high work function, thus suffer from the same issue of slow consumption of photogenerated holes. Adding TEOA then accelerates this half-reaction, increases the overall reaction rate, and speeds up the motor.

TEOA is, however, not effective when hole scavengers are not useful. For example, we show in Fig. 4c that neither TEOA, nor ethanol or H$_2$Q, is an effective fuel for a Cu$_2$O–Au micromotor (Video S4, ESI†). This is because Cu$_2$O is a p-type semiconductor, and when forming a heterojunction with Au the electrons at the metal end will flow to the semiconductor, causing the Cu$_2$O/water interface to be dominated by reduction (exactly the opposite to TiO$_2$–Pt). To improve the performance of a Cu$_2$O motor, electron scavengers rather than hole scavengers are needed, which makes H$_2$O$_2$ or BQ, rather than TEOA or H$_2$Q, an effective fuel for Cu$_2$O–Au motors. Moreover, TEOA is not useful for SiO$_2$–TiO$_2$ micromotor either (Fig. 4d), made by half-coating a silicon dioxide (SiO$_2$) microsphere with TiO$_2$ (see ESI† for details on sample preparation). In this case, the photocurrent is limited not by one of the two half-reactions, but by high recombination between photoelectrons and holes. Therefore, redox shuttles such as H$_2$O$_2$ or the BQ/H$_2$Q pair are effective fuels for SiO$_2$–TiO$_2$ motors because they improve the reaction on both the photocathode and anode (shown in Video S5, ESI†).

In conclusion, we have demonstrated that the speed of photocatalytic TiO$_2$–Pt micromotors can be significantly improved by an aqueous solution containing mM triethanolamine (TEOA), reaching $\sim 35 \text{ mm s}^{-1}$ at 0.5 mM under 650 mW cm$^{-2}$ UV irradiation. Additional advantages of this new fuel molecule include a small operating concentration that is 4 orders of magnitude lower than other common fuels, a minimal effect of bubbles even after tens of minutes of operation or with a large motor population, as well as the ability to move in salt solutions up to 5 mM concentration. The excellent performance of TEOA as fuel for photocatalytic motors is due to its fast deprotonation as it scavenges photogenerated holes, accelerating the reaction kinetics at the TiO$_2$ surface. This TEOA-mediated acceleration can be extended to other photocatalytic micromotors made of n-type semiconductors (such as TiO$_2$ and ZnO), but not those made of p-type (e.g. Cu$_2$O) or without a metal-semiconductor interface. Beyond the discovery of a highly effective fuel molecule, this study also highlights the thermodynamic and kinetic principles in designing efficient photocatalytic micromotors.

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Conflicts of interest
There are no conflicts to declare.

Notes and references

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