Carbon-Dot-Induced Acceleration of Light-Driven Micromotors with Inherent Fluorescence

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Real-time visualization of the positions of micro/nanomotors is highly desired for practical applications due to the complex environments that they are used in. However, most reported photocatalytic micromotors can only be tracked in transparent solutions under bright fields, which greatly limits their applications. Herein, photocatalytic micromotors based on Cu$_2$O@carbon dot (CDot) particles with excellent fluorescent properties and precise propulsion capabilities in 3D are reported. In the fully green environment of malic acid, the Cu$_2$O@CDot micromotors display efficient propulsion under visible light irradiation (as high as 40.85 μm·s$^{-1}$). In addition, the propulsion direction of the Cu$_2$O@CDot micromotors can be effectively adjusted by changing the direction of light via positive phototaxis. Interestingly, due to the presence of CDots, these new Cu$_2$O@CDot micromotors display excellent and stable fluorescence. This study reports the first photocatalytic micromotors with both novel fluorescence properties and excellent propulsion characteristics in biocompatible environments. Due to their excellent fluorescent properties and precise motion control, these Cu$_2$O@CDot micromotors hold great potential to perform complex tasks across diverse practical applications.

Micro/nanomotors, which can exhibit autonomous self-propulsion by harnessing energy and can perform specialized tasks in microscopic environments, have attracted intensive study across many areas of science. Until now, a number of micro/nanomotors have been developed, such as metallic nanomotors, semiconductor-based micro/nanomotors, polymeric-based swimmers, and metal-organic frameworks-based micromotors, which achieve propulsion through a variety of different mechanisms. Among these, photocatalytic micro/nanomotors are one of the most studied micro/nanomotors since they can efficiently move using various fuels by harnessing photocatalytic reactions to convert both optical and chemical energy to power the motor’s mechanical movement. Due to their excellent controllable motion performance and their functional versatility, these photocatalytic micro/nanomotors have been successfully applied for a variety of fields ranging from environmental remediation to biological applications and nanomedicine.

Photocatalytic nanomaterials are expected to provide new opportunities for the synthesis of photocatalytic micro/nanomotors. Cuprous oxide (Cu$_2$O), a common photocatalyst, has excellent visible light (<700 nm) photocatalytic properties. It is well demonstrated that Cu$_2$O is an ideal candidate for the photocatalytic degradation of a wide range of fuels which can provide substantial power for the motor’s movement. However, single-component Cu$_2$O micro/nanomotors usually exhibit weak propulsion due to the low photocatalytic efficiency. As a result, numerous strategies have been employed to enhance the photocatalytic efficiencies of Cu$_2$O and to further improve the photocatalytic propulsion of the corresponding motors, such as coating gold, doping carbon nanotubes, and inducing defects. Such reported motors can be efficiently propelled under visible light; however, the ideal artificial micro/nanomotors with excellent motion control should have two critical properties: efficient propulsion and precise direction control. To control the direction of the motors, real-time visualization of the positions of the micro/nanomotors is crucial to tune the parameters of the external stimuli and to efficiently regulate the motors’ motion direction. However, all of the reported Cu$_2$O-based photocatalytic micromotors can only be tracked in transparent solutions under bright fields. Therefore, developing synthetic photocatalytic micro/nanomotors with efficient propulsion, responsive direction control, and specific properties for motion tracking in complicated microenvironments is still a great challenge.

Carbon dots (CDots), as a fantastic carbon nanomaterial recently reported, display semiconductor-like photobleaching properties, photoinduced electron transfer, luminescence, and so on. Due to their excellent electron-transfer efficiency, intense photoluminescence, distinct structure, and tunable light-harvesting range, CDots have demonstrated excellent performance in a wide variety of fields, such as photoelectrochemical
and photocatalytic applications.\textsuperscript{[30]} Accordingly, the integration of CDots into the Cu$_2$O body may provide a potential way to fabricate photocatalytic nanomotors that have both novel fluorescence properties and excellent propulsion characteristics in biocompatible environments.

In this study, a novel photocatalytic micromotor of a Cu$_2$O@CDot particle (=1.5 μm mean diameter) with excellent fluorescence property and optically regulated direction of propulsion is reported. Malic acid, a biocompatible molecule either found in biomass or produced in various degradative processes, was chosen as the fully green fuel. As shown in Scheme 1, in the fully green environment of malic acid, Cu$_2$O@CDot micromotors display efficient propulsion under visible light irradiation (as high as 40.85 μm s$^{-1}$). In addition, the propulsion direction of the Cu$_2$O@CDot micromotors can be effectively directed by adjusting the direction of the light sources (moving toward the light sources). These new Cu$_2$O@CDot micromotors demonstrate excellent and stable fluorescence due to the presence of CDots. Such Cu$_2$O@CDots, which can be driven in the fully green environment of malic acid by visible light and have excellent fluorescence properties, hold considerable promise for designing controllable and intelligent “robots” to perform specialized tasks across diverse practical applications.

This synthesis technique allows for one-pot preparation of the Cu$_2$O@CDot micromotors, which is simple and repeatable. To briefly summarize, CDots, sodium dodecyl sulfate (SDS), copper acetate, sodium hydroxide, and glucose were dissolved in an ethanol aqueous solution, and then the reaction was maintained for 30 min at 73 °C. After that, the obtained brick-red solution was washed with deionized water five times by centrifuging at 5000 rpm for 5 min and then dried at 60 °C in vacuum, resulting in the Cu$_2$O@CDots. The size and morphology of Cu$_2$O@CDot micromotors were primarily characterized by scanning electron microscopy (SEM). As shown in Figure 1A, the inset SEM image confirms that the particle size distribution of these prepared Cu$_2$O@CDot micromotors has approximately an average size of 1.5 μm and a relatively uniform spherical shape. Importantly, the surface protruding structure can be clearly seen in the inset SEM image. In addition, as shown in Figure 1A, the structure of Cu$_2$O@CDots is well characterized by X-ray powder diffraction (XRD), where it is shown that all diffraction peaks are characteristic of the orthogonal Cu$_2$O. It is important to note that

![Scheme 1](image)

**Scheme 1.** A) The propulsion mechanism of the Cu$_2$O@CDot micromotors in the solution of malic acid under green light. B) The trajectory over 3 s of Cu$_2$O@CDot micromotors with horizontal visible light in the solution of 0.025 mM malic acid (taken from Video S2, Supporting Information). C) The fluorescent field image of Cu$_2$O@CDot micromotors. Scale bar: 10 μm.

![Figure 1](image)

**Figure 1.** A) The XRD pattern of Cu$_2$O@CDot micromotors (inset: the SEM image of Cu$_2$O@CDot micromotors). B) The SEM image of a single Cu$_2$O@CDot micromotor. C–E) The corresponding EDX mapping images for Cu, O, C, respectively. F,G) TEM image of the Cu$_2$O@CDot micromotor. H) HRTEM image of the Cu$_2$O@CDot micromotor.
the corresponding characteristic peaks of CDots are not obviously observed in XRD, due to the low content of CDots, while the existence of CDots has been adequately confirmed by SEM and energy-dispersive X-ray spectroscopy (EDX) characterization. The SEM image of Figure 1B indicates the morphology of an obtained Cu2O@CDot micromotor, which further demonstrates that CDots are well distributed on the surface of the Cu2O microsphere. The corresponding EDX mapping of Cu, O, and C shown in Figure 1C,D,E further confirms the crystal structure of the obtained Cu2O@CDot micromotor. In addition, the structure of the Cu2O@CDots have also been characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Figure 1F,G, the TEM image of the Cu2O@CDot composite shows a perfect crystalline structure with the Cu2O doped with CDots. Furthermore, as shown in the HRTEM image (Figure 1H), the lattice spacing of about 0.25 nm is in good agreement with the crystallography <111> Cu2O spacing and the lattice spacing of about 0.32 nm is consistent with the crystallography <002> carbon spacing, indicating that CDots have been successfully loaded with the particle of Cu2O. Therefore, the structure of Cu2O@CDots has been solidly confirmed through the aforementioned results.

In this system, due to the limited penetration depth of irradiated light in Cu2O@CDots micromotor, asymmetrical surface photocatalysis reactions are conducted on the isotropic semiconductor particles, resulting in a large number of products on the irradiated side. Thus, a concentration gradient is produced across the Cu2O@CDot micromotors, which subsequently results in the active motion of the micromotors via self-diffusiophoresis, in which the motion of particles is driven by the concentration gradient. As schematically shown in Scheme 1, with the irradiation of visible light on one side of the micromotors, photo-generated electrons and holes are formed within Cu2O@CDot micromotors. Significantly, the presence of CDots causes electrons to transfer from the Cu2O conduction band to the CDots, which greatly hinders the charge recombination. The separated and stabilized charges account for the strong photocatalytic activity. In the solution of malic acid, the malic acid is decomposed with the generated holes and the charges, which forms a concentration gradient around the motor surface and further provides sufficient power for the active motion of the Cu2O@CDot micromotors. According to the classic metal-oxide photocatalyst photocatalytic mechanisms, the oxidation of malic acid proceeds according to a photo-Kolbe reaction:

\[
RCOO^- + h^+ \rightarrow R + CO_2 \tag{1}
\]

and OH• radicals are prone to abstract an H atom:

\[
RCOO^- + OH \rightarrow R - COO^{-} + H_2O \tag{2}
\]

The Cu2O@CDot micromotors exhibit attractive photocatalytic propulsion in the solution of malic acid under 55 300 lux green light, and the speed of Cu2O@CDot micromotors can be easily regulated by adjusting the concentration of malic acid. As shown in Figure 2, due to the lack of chemical fuels, the micromotors can be driven weakly in pure water (about 5.24 μm s\(^{-1}\)). Excitingly, with the addition of malic acid, the speed of the motor increases significantly with increasing concentrations of malic acid within the range 0–0.05 mM. At concentrations of malic acid as low as 0.0125 mM, the speed of the motor can be increased to 30 μm s\(^{-1}\). As the concentration is increased to 0.025 mM, the speed of the Cu2O@CDot micromotors can reach up to the maximum speed of 40.85 μm s\(^{-1}\), which is two times faster than the speeds of presently reported glucose-fueled Cu2O@N-doped carbon nanotube micromotors also under 55 300 lux visible light, and is 26 times faster than that of previously reported micromotors that are propelled by water under visible light of similar intensity. Furthermore, when compared with H2O2-fueled motors, the green fuel of Cu2O@Cdot micromotors is much more biocompatible when used at lower concentrations. However, it is noted that when the concentration of malic acid is further increased past 0.025 mM, the speed of the motor gradually decreases. For example, when the concentration of malic acid is increased to 0.5 mM, the speed of the motor is reduced to 30.2 μm s\(^{-1}\). This is most likely because the strength of the concentration gradient around the micromotors is weakened due to the high concentration of malic acid. As shown in Figure 2B, the speeds of the motors can be confirmed by the corresponding tracklines over 3 s of micromotors in 0, 0.0125, 0.025, and 0.01 mM malic acid solutions under green light.

![Figure 2](https://www.advancedsciencenews.com)

**Figure 2.** A) Velocity of Cu2O@CDot micromotors in different concentrations of malic acid solutions under 55 300 lux visible light and B) the corresponding trajectories over 3 s of micromotors (taken for Video S1, Supporting Information). Scale bar: 10 μm.
Interestingly, the Cu$_2$O@CDot micromotors can achieve directional motions in the solution of malic acid in a 3D space by adjusting the direction of light. Similar to the phototaxis of green algae, the as-prepared Cu$_2$O@CDot micromotors can also mimic the positive or negative phototaxis behaviors by taking advantage of different light-induced chemical propulsion mechanisms. Generally, the propulsion of the Cu$_2$O@CDot micromotors in the solution of malic acid is mainly due to light-induced self-diffusiophoresis, which primarily includes diffusiophoresis, osmophoresis, and chemophoresis. It is noted that the electrolyte gradient causes a chemophoretic flow with the direction opposite to that of osmophoresis, which corresponds to the positive and negative phototaxis, respectively.\[36\] In this system, as discussed previously, the products contain not only neutral molecules but also cationic and anionic species (HCOO$^{-}$, H$^{+}$).\[33\] Therefore, there could be two distinct types of possible propulsion mechanisms in this system. To explore the dominant mechanism, first, the propulsion of the micromotors was tested in the solution of malic acid (0.025 mM) under horizontal green light. As shown in Figure 3A,B, the micromotors move toward the light source and the performed apparent positive phototaxis. The result impressively demonstrates that the propulsion mechanism is dominated by the chemophoretic propulsion. Due to their excellent positive phototactic behavior, the visible light-driven motors exhibit efficient direction control by light regulation. As shown in Figure 3B and Video S2, Supporting Information, the motors move toward the light when on and immediately stop with the light off. By adjusting the direction of the incident light, the motion direction can be easily controlled. Taken together, when compared with other micro/nanomotors, the Cu$_2$O@CDot micromotors exhibit a significant advantage in motion controllability, which is convenient, repeatable, and efficient.

Apart from that, the Cu$_2$O@CDot micromotors can also display apparent vertical motion in the solution of malic acid under high-energy visible light. As can be seen in Figure 3C, initially, the layer of micromotors is focused. However, when the light is turned on from the bottom of the slide, the focus of the Cu$_2$O@CDot micromotors in the bright field becomes gradually blurred. This is due to the vertical movement of the Cu$_2$O@CDot micromotors, which move out of the plane of focus. The focal plane of the microscope must be readjusted in the new layer of the solution. Time-lapse images of the vertical motion are shown in Figure 3D. The Cu$_2$O@CDots micromotors could counterbalance their gravity and demonstrated a fast response to the vertical light, which can be explained in detail by the previously reported mechanism of photogravitacticity. In brief, when the light energy is higher than the gravity-related threshold, the motors can be propelled in a vertical direction. Conversely, when the light intensity is lower than the threshold value, the motors only displays horizontal motion (as shown in Figure 2) even if the light is still from the bottom and perpendicular to the substrate. Therefore, the high-energy blue light irradiated from the bottom can cause the vertical movement of the Cu$_2$O@CDot micromotors. Due to the facile and precise control of the motion speeds and trajectories, the attractive 3D motion of such micromotors may provide new capabilities for the design of smart microsubmarines for specific tasks.

The reported Cu$_2$O@CDot micromotors are endowed with excellent fluorescence characteristics due to the incorporation of CDots. As shown in Figure 4, even after the synthetic Cu$_2$O@CDot micromotors are stored for more than four weeks, the strong green fluorescence of the Cu$_2$O@CDot micromotors can be clearly observed under excitation by blue light. However, no fluorescence can be observed with pure Cu$_2$O. Impressively, the fluorescence of the Cu$_2$O@CDot micromotors is bright, stable, and perfectly uniform. Currently, most reported fluorescent micro/nanomotors are generally realized by modifying fluorescent molecules or fluorescent materials onto their surface, which is laborious and time consuming.\[37,38\] In addition, even after

![Figure 3](image1.png)

**Figure 3.** A) Schematic of the horizontal motion of a Cu$_2$O@CDot micromotor in the solution of malic acid (0.025 mM) under horizontal green light. As shown in Figure 3A,B, the micromotors move toward the light source and the performed apparent positive phototaxis. The result impressively demonstrates that the propulsion mechanism is dominated by the chemophoretic propulsion. Due to their excellent positive phototactic behavior, the visible light-driven motors exhibit efficient direction control by light regulation. As shown in Figure 3B and Video S2, Supporting Information, the motors move toward the light when on and immediately stop with the light off. By adjusting the direction of the incident light, the motion direction can be easily controlled. Taken together, when compared with other micro/nanomotors, the Cu$_2$O@CDot micromotors exhibit a significant advantage in motion controllability, which is convenient, repeatable, and efficient.

![Figure 4](image2.png)

**Figure 4.** Characterization of the fluorescent property of Cu$_2$O@CDot micromotor. Bright-field image (left), fluorescence image (middle), and their merge (right) of Cu$_2$O@CDot micromotor and Cu$_2$O, respectively. Scale bar: 10 μm.
successful modification, there are frequently encountered problems, including unstable motor fluorescence and heterogeneous brightness. Furthermore, these processes can also reduce the speeds of the micro/nanomotors. Compared with other fluorescent micro/nanomotors, Cu₂O@CDots micromotors offer several distinct advantages. First, the one-step method for the preparation of Cu₂O@CDots is convenient, facile, and low cost, and they can be batch produced, which provides a favorable foundation for further applications. Second, due to the superior fluorescent property of CDots, the obtained Cu₂O@CDot micromotors are endowed with highly stable and consistent fluorescence, which makes them less susceptible to changes of environment, such as the catalogues, concentrations, pH, and ionic strength of the medium. This, to some extent, makes it possible to observe the movement state of the micromotors in complex environments. Due to these advantages, Cu₂O@CDot micromotors have great potential for applications in the field of nanomedicine, for example, in cell imaging and biological detection. More importantly, the resulting Cu₂O@CDot micromotors have outstanding uniformity and perfect monodispersity, demonstrating the high efficiency of our method and promising great advantages for their further application. Due to the aforementioned superior advantages of Cu₂O@CDot micromotors, we believe that such Cu₂O@CDot micromotors may be beneficial for potential biomedical applications and they can be used to perform specialized tasks.

In conclusion, we have reported the facile one-step fabrication of novel photocatalytic micromotors of Cu₂O@CDots that can be powered in the fully biocompatible fuel malic acid and are endowed with excellent fluorescence properties. The Cu₂O@CDot micromotors can generate strong propulsion forces from the photocatalytic decomposition of malic acid, with a speed as high as 40.85 μm s⁻¹ under green light. The enhanced photocatalytic activity of Cu₂O@CDots benefits from the collective effect of the superior light-reflecting ability of the Cu₂O protruding nanostructures and the unique property of CDots. In addition, we have demonstrated that the direction of the micromotors can be regulated through 3D space with excellent on/off characteristics by adjusting the direction of the light sources (moving toward the light sources). Significantly, we demonstrate for the first time that these photocatalytic micromotors display excellent and stable fluorescence due to the presence of CDots. Compared to other photocatalytic micromotors, the micromotors of Cu₂O@CDots described here hold considerable promise for designing smart “robots” that are meant for future practical applications.

**Experimental Section**

**Synthesis of Cu₂O@CDot Micromotors:** The CDots were synthesized according to a previous report. First, 0.2 g of carbon fiber powder (purchased from Shanghai Tansu Plant) was added to a solution of 10 M nitric acid and then refluxed for 4 h. After that, the resulting solution was collected and the pH of the solution was adjusted to about 3 with NaHCO₃. Subsequently, the solution was filtered through a 0.22 μm BIOSHARP membrane filter and further dialyzed for 7 days in deionized water (18.2 MΩ cm) with a 3500 Da dialysis bag. Finally, the solution was subjected to ultrafiltration with 100, 50, 30, 10, and 3 kDa centrifugal filters (Millipore), in this order. As a result, CDots < 3 kDa were obtained. Next, 2.5 mg of the prepared CDots were dispersed in 14 mL of ethanol (Damao Chemical Reagent Factory) and ultrasonic pretreatment was conducted for 2 h for subsequent preparation application. For the synthesis of Cu₂O@CDots, in short, first, SDS (0.4 g) (Acros #151-21-3) and copper acetate (0.2 g) (Aladdin #C105398) as well as 8 mL deionized water (18.2 MΩ cm) were added into a round bottom flask. After all the substances had dissolved, 8 mL of ethanol dispersion containing CDots was immediately added into the round bottom flask. Afterward, the flask was placed back in the oil bath and when the temperature maintained at 73 °C, 0.28 g of sodium hydroxide (Tianjin ZhongReagent Co, Ltd) and 0.24 g of glucose (RichJoint Chemical) were added, and then the reaction was allowed to stand at 73 °C for 30 min. The obtained orange Cu₂O@CDot microspheres were washed with deionized water (18.2 MΩ cm) five times, which was followed by desiccation at 60 °C in vacuum. Finally, Cu₂O@CDot micromotors (diameter ≈1.5 μm) were obtained.

**Motion Calibration Experiments:** The active propulsion of the Cu₂O@CDot micromotors in different concentrations of malic acid was obtained as follows: first, 1 μL of Cu₂O@CDot micromotors dispersed in deionized water and 1 μL of malic acid were mixed, and then they were dropped on a slide to track the motion state by an inverted optical microscope (Nikon Instruments Inc. Ti-S/L100 dynamic state). Videos were captured by an inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with 40× objectives, and a Hamamatsu ORCA-flash 4.0 LT (C11440) sCMOS digital camera. At each condition, 30 motors, which were randomly selected, were analyzed. The trajectories and the velocities of the motors were obtained by the NIS-Elements AR 4.3 software. The direction control of the Cu₂O@CDot micromotors in the horizontal direction was achieved by placing a green light source on one side of the substrate.

**Equipment:** SEM patterns were attained by a TESCAN MAIA 3 and XRD patterns were obtained by an X-ray diffractometer (Bruker D8 ADVANCE, Germany). Visible light was generated from Mercury lamp sockets and a dichroic mirror DM 400. A barrier filter BA520 was used to generate blue light and a barrier filter BAS90 for green light. Videos were captured by an inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with 40× objectives, and a Hamamatsu ORCA-flash 4.0 LT (C11440) sCMOS digital camera using the NIS-Elements AR 4.3 software.

**Supporting Information**

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

**Acknowledgements**

J.W., H.W., and R.D. contributed equally to this work. The authors are grateful to the National Natural Science Foundation of China (21805096, 21671071), Natural Science Foundation of Guangdong Province (2018A030313358, 2017A030310432), Characteristic Innovation Projects of Guangdong Ordinary University (2018KTSCX045), Applied Science and Technology Planning Project of Guangdong Province (2015B010135009, 2017B090917002), Innovation Team Project of Guangdong Ordinary University (2015KXDT0005), The Great Scientific Research Project of Guangdong Ordinary University (2016KZDKM023), and Research and Training Fund for Young Teachers of South China Normal University (No. 18KJT3).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

carbon dots, Cu₂O, malic acid, micro/nanomotors, visible light.
