Design and Control of Bioinspired Millibots

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In the last decade, there has been great progress in the field of smart materials and technologies for the development of bio-inspired artificial insects. An insect-mimetic functional nanocomposite, namely, millimeter-sized robot (millibot), based on magnetite, zeolitic imidazolate framework-8, and polytetrafluoroethylene is successfully prepared. The millibots are designed through a rational chemical design for controlling its multi-functions by external light and magnetic field, which act as fuels. The millibots can be effectively loaded with CO$_2$ gas and remotely controlled by photothermal energy for the release of CO$_2$ molecules from the laser-induced millibots to anesthetize fruit flies as a potential foreign enemy. A remote regulation of the photo- and magnetic field-induced millibot dynamic locomotion is demonstrated. As a proof of principle, millibots equipped with a gelatin particle encapsulating rhodamine B are efficaciously used in the bio-inspired spawning of an artificial insect. The materials and strategies could inspire new designs for the development of high-performance biologically active insect-type robots in the future.

Natural insects have acquired various intelligent functions such as mimicking ability, parasitism, and a wide variety of attacking ways against enemies, during their evolution processes over the course of a billion year.[1,2] The study of fundamental principles of insect materials, structures, functions, and behavior is of major scientific interest.[3,4] In addition, it is substantially interesting to develop biomimetic materials and engineering features from the unique functions of insects.[5,6] Indeed, many researchers have successfully created insect-mimetic smart materials and technologies providing optical-tunable devices, flight insect-scale robots, and self-propelled autonomous machines.[7–15] There is still a great interest in understanding and achieving remote manipulation of bio-inspired insects. In addition, the exploration of diverse functionalities and controllable locomotive actions of artificial insects could be also a milestone for integrating these new types of robots with numerous applications.

In the current study, we explored an approach for chemical design and control of synthetic insects called millimeter-sized robots (millibots) by integrating functional materials. These chemical and materially engineered insect-mimetic millibots demonstrated various unique properties including anesthetizing of a fruit fly, thermal and magnetic locomotion at the air–water interface, and artificial spawning by external stimuli. Our findings will contribute to the development of next-generation biomimetics for various applications.

To construct artificial insect millibots, we first used multifunctional materials including magnetite (MAG), zeolitic imidazolate framework-8 (ZIF-8) nanocrystal, and polytetrafluoroethylene (PTFE) (Figure 1). MAG was selected as a model photo-thermical and magnetic material due to its strong photothermal conversion effect and ferromagnetism.[16,17] A porous metal–organic framework (MOF); ZIF-8 can work as a representative CO$_2$ gas absorber,[18,19] and we expect that it will be able to control absorption and desorption of CO$_2$ gas by external stimuli for controlling the function of prepared synthetic insects. The successful formation of synthesized ZIF-8 nanocrystals was proven by the X-ray diffraction (XRD) pattern (Figure S1a, Supporting Information).[20] The transmission electron microscopy (TEM) observation exhibited a rhombic dodecahedral morphology (Figure S1b, Supporting Information).[21] The diameter of the nanocrystals was determined as 40.97 ± 3.57 nm (over 150 particles). PTFE[22,23] was chosen to improve the mechanical stability and water repellency of the nanocomposite. MAG–ZIF-8–PTFE nanocomposites were easily prepared by a mechanical compressive pill maker. As we expected, the formability of a nanocomposite material had excellent moldability and a self-standing feature due to the high plasticity of PTFE molecules, which allows their shapes to be simply fabricated by a metal hole-puncher (Figure S2a, Supporting Information). A nanocomposite without PTFE was mechanically unstable and broke easily after taking out from a pill maker (Figure S2c, Supporting Information).

Scanning electron microscopy (SEM) of a nanocomposite showed a relatively flat surface structure because it was prepared by high compression (Figure S3, Supporting Information). Meanwhile, energy dispersive X-ray spectroscopy (EDS) clearly identified elemental ingredients such as carbon, zinc, iron, fluoride, and oxygen in the nanocomposite (Figure S3, Supporting Information).

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Pheropsophus jessoensis (Morawitz) is an Asian beetle which can spray hot gas composed of water vapor and benzoquinone, that are produced by hydrogen peroxide and hydroquinone in their body when they are attacked by an enemy (Figure 2a). Thus, we got inspired by this aggressive gas-releasing behavior of P. jessoensis (Morawitz) as the first example of an artificial insect using near-infrared (NIR) laser and CO$_2$ gas-filled nano-composite (Figure 2b). ZIF-8 can effectively absorb and desorb CO$_2$ gas. The prepared nanocomposite based on PTFE, MAG, and ZIF-8 can thus adsorb and desorb CO$_2$ gas at ambient temperature ($\approx 20^\circ$C) under atmospheric pressure ($\approx 101$ kPa) (Figure 2c). About 2.4 wt% of CO$_2$ gas was able to be incorporated in a 3 mm diameter and 1 mm thickness of nanocomposite ($\approx 7.5$ mg) after loading under ambient condition. CO$_2$ gas was repeatedly released by an 808 nm NIR laser irradiation at 440 mW ($\approx 22.4$ mW mm$^{-2}$) just for 2 s (Figure 2d).

Figure 1. Photograph of a prepared MAG–ZIF-8–PTFE nanocomposite disk (left) and a schematic illustration of chemicals in the nanocomposite (right).

Figure 2. Biomimetic P. jessoensis (Morawitz). a) Photograph of P. jessoensis (Morawitz). b) Concept of CO$_2$ gas releasing from NIR-laser-induced nanocomposite. c) Experimental CO$_2$ adsorption–desorption isotherms in the nanocomposite at 20 °C. d) Continuous CO$_2$ gas releasing profile from the nanocomposite by NIR laser irradiation. e) Thermographic image of laser-induced nanocomposite. f) Anesthesia of wingless fruit fly by laser-driven biomimetic P. jessoensis (Morawitz).
Released gas was gradually reduced by continuous laser irradiation at each step probably because the amount of CO\textsubscript{2} stored is steadily consumed from a nanocomposite by repeated laser illumination. On the other hand, we expect that CO\textsubscript{2} molecules entrapped in ZIF-8 were thermally diffused and eventually escaped to the outside of a nanocomposite via the thermal desorption process\cite{25}, due to the photothermal property of MAG (Table S1, Supporting Information). Another possibility is that CO\textsubscript{2} molecules might be forcefully desorbed due to thermal decomposition of ZIF-8, although it has high heat-resisting temperature (\textasciitilde300°C)\cite{26}. Thermographic camera showed that the surface temperature of the composite was achieved at around 101°C by laser irradiation for 1 min (Figure 2e). Therefore, we believe that CO\textsubscript{2} was mainly released by conventional thermal desorption process without a drastic structural decomposition of ZIF-8\cite{27}. To the best of our knowledge, this is the first demonstration of a gas releasing from a MOF attributed to biologically permeable NIR light-triggered photothermal effect of a material acting as the driving force, although MOFs themselves have been frequently used as an engine to locomote small objects by releasing simple substrates from MOFs\cite{28}.

We also confirmed that other composites based on the different type of photoexothermal nanoparticles had a flat surface structure and sufficient elemental concentration by SEM and EDS, respectively (Figure S3, Supporting Information). These nanocomposites also exhibited photothermal property in a similar nature to MAG–ZIF-8–PTFE by laser irradiation (Table S1, Supporting Information). Nevertheless, we used MAG as one of the components in nanocomposite for further experiments because MAG not only possesses powerful photothermal property but also natural magnetic feature to provide an artificial insect multifunctionality.

Inspired by the laser-triggered CO\textsubscript{2} gas-releasing phenomenon, we observed that the laser-tunable effective CO\textsubscript{2} gas emission of a composite could anesthetize a wingless fruit fly (Drosophila melanogaster) in a 323 μL small volume well after laser irradiation for about 1 min at the power of 440 mW (22.4 mW mm\textsuperscript{-2}) (Figure 2f and S5, Video 1, Supporting Information). The treated flies started moving again after laser irradiation was discontinued and the glass slide covering the well was removed (Video 2, Supporting Information). In addition, the control nanocomposite without CO\textsubscript{2} loading could not anesthetize flies at all (Video 1, Supporting Information). This is probably because CO\textsubscript{2} acts as the dominant force for anesthesia of flies rather than heat generation. In fact, CO\textsubscript{2} gas is often used to anesthetize experimental animals including fruit fly\cite{29}. Thus, fruit flies could sleep in a well after CO\textsubscript{2} gas released from the laser-induced nanocomposite. In addition, the flies unfortunately died once they accidentally climbed on the laser-induced and heated composite with or without CO\textsubscript{2} loading due to the strong photothermal property of a composite, although we carefully irradiated the composite when the fly was separated from a composite as shown in Figure 2f. Fruit flies did not sleep at all by other composite ratios (MAG:ZIF-8:PTFE = 1:1:1 or 1:5:1) probably because the essential CO\textsubscript{2} gas for anesthetizing an insect was effectively loaded and released when the composite was mixed at the 1:10:1 ratio.

![Figure 3](https://www.advancedsciencenews.com)

**Figure 3.** Synthetic A. paludum. a) Photograph of A. paludum. b) NIR-laser-driven dynamic motion of biomimetic water strider. The white line shows the path of the nanocomposite. c) Magnetic locomotion of biomimetic water strider.
Water strider *Aquarius paludum* can smoothly walk above water by applying water-resistant hair which has lower surface tension than water (Figure 3a). MAG–ZIF-8–PTFE nanocomposite could float on the water surface because of the water repellency of PTFE. Thermal convection derived from powerful photothermal property of laser-induced nanocomposite can cause dynamic motion of a small disk (3 mm of diameter and 1 mm of thickness) at air–water interface such as *A. paludum* (Figure 3b and Video 3, Supporting Information). In fact, a temperature gradient can cause a surface-tension gradient (thermal convection), which will naturally cause the liquid to flow away from regions of low surface tension, thus leading to the spontaneous movement of the surface (Figure S4, Supporting Information). The directional movement of the composite was fully controllable by chasing a disk with a laser beam on the water surface (see Video 3, Supporting Information).

Interestingly, the velocity of the CO₂-filled MAG–ZIF-8–PTFE nanocomposite (2.6 cm s⁻¹) was slightly decelerated than that of the control nanocomposite without CO₂ (2.9 cm s⁻¹) due to the increase in weight by CO₂ loading into the composite. In other words, this deceleration effect proved that the prepared nanocomposites could surely deliver CO₂ molecules at the air–water interface. Herein, we consider that CO₂ gas was not released from the composite during laser-driven movement probably because the photothermally heated composite for triggering CO₂ emission could be cooled down by the heat of water vaporization at the surface.

In addition, dynamicity of a nanocomposite disk was also fully controllable by simply getting closer a neodymium magnet to the nanocomposite due to the strong ferromagnetic property of MAG (Figure 3b and Video 4, Supporting Information). The speed of the magnetic field-applied...
nanocomposite was about 11.4 cm s\(^{-1}\). These results clearly displayed that both photothermal- and magnetic field-induction could provide an inorganic nanocomposite attractive dynamic characteristics such as a living water strider that can actively skate on the water surface.

Finally, the aforementioned multifunctionality of nanocomposites was compiled to inspire the natural biological activity of ferocious water bug (Figure 4). Spawning is one of the most important insect ecology in addition to predatory or protective attacks from a foreign enemy as we have demonstrated. A combination of magnetic-locomotion and laser-triggered exothermic behavior was applied to explore artificial spawning for the prepared biomimetic *Appasus japonicus* (Figure 4a,b). A temperature-responsive gelatin particle encapsulating pink-colored rhodamine B (RhB) molecules was utilized as a model synthetic egg and mounted onto a 10 mm diameter and 2 mm thickness of MAG–ZIF-8–PTFE nanocomposite disk. Sticky gelatin particle was immovable on a nanocomposite and could be stably attached even after quick magnetic locomotion (8.3 cm s\(^{-1}\)) (Video 5, Supporting Information). RhB was effectively released at the desired position on water surface just after laser irradiation with power of 440 mW (22.4 mW mm\(^{-2}\)) (Figure 4c and Video 5, Supporting Information). Amount of releasing of RhB molecules was regulated over irradiation time (Figure 4d). Indeed, it is well known that thermal degradation of gelatin networks (sol–gel reaction) occurs at more than 40 °C.\(^{[\text{16}]}\)

The previously described potent exothermic property of the laser-triggered nanocomposite is sufficient to decompose gelatin particles. These results unambiguously indicated that artificial spawning was spatiotemporally succeeded by a combination of highly controllable magnetic field and laser induction.

In summary, laser- and magnetic field-driven highly performing artificial insect millibots, based on MAG, ZIF-8, and PTFE were developed. We succeeded in synthesizing millibots with effective CO\(_2\) gas releasing, strong magnetic characteristics and powerful photothermal properties, enabling anesthesia of fruit fly and spatiotemporal controlled release of substrates from the nanocomposites at the desired location on the water surface, using a NIR laser and a magnet in a non-contact manner. To the best of our knowledge, this represents the first demonstration of remotely controlled gas expression, thermal and magnetic locomotion that relies on the application of a strong magnetic field, and powerful photothermal and gas-controlled-release properties of combined functional materials. Amid these dynamic motions, magnetic locomotion of a nanocomposite might require a remote “closed-loop” control system for future applications. But we believe that the system allows versatile multi-locomotion model which is fully controllable rather spontaneous self-propelled objects. In addition, combining the laser- and magnetic field-driven dynamic locomotion of the millibot and the gas expression using MOF together, on-demand directional and complicated robotic outputs of the millibot might be readily obtained, showing promise for miniaturized units for potential applications in molecular transportation systems in comparison with the biomimetic robots considering other types of self-propelled swimmers and driving objects by gas evolution. Controlled designing of millibots represent a promising technology for use in materials science and biological application. In addition, the use and development of synthetic biology would be scientifically valuable to better understand living organisms. At least, the application of substrates releasing from a nanocomposite by external stimuli could be useful for advanced drug delivery systems for future biomedical applications.

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

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Conflict of Interest
The authors declare no conflict of interest.

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