Research paper

Visible light triggered exfoliation of COF micro/nanomotors for efficient photocatalysis

Kai Feng a,1, Liang Zhang b,1, Jiang Gong a,**, Jinping Qu a,c, Ran Niu a,*

a Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Engineering Research Center for Bionanomaterials and Medical Protective Materials, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China

b The State Key Laboratory Breeding Base of Basic Science of Stomatology (Hubei-MOST) & Key Laboratory of Oral Biomedicine Ministry of Education, School and Hospital of Stomatology, Wuhan University, Wuhan 430079, China

c National Engineering Research Center of Novel Equipment for Polymer Processing, Key Laboratory of Polymer Processing Engineering, Ministry of Education, Guangdong Provincial Key Laboratory of Technique and Equipment for Macromolecular Advanced Manufacturing, School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou, 510641, PR China

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Abstract

We report a new facile light-induced strategy to disperse micron-sized aggregated bulk covalent organic frameworks (COFs) into isolated COFs nanoparticles. This was achieved by a series of metal-coordinated COFs, namely COF-909-Cu, -Co or -Fe, where for the first time the diffusio-phoretic propulsion was utilized to design COF-based micro/nanomotors. The mechanism studies revealed that the metal ions decorated in the COF-909 backbone could promote the separation of electron and holes and trigger the production of sufficient ionic and reactive oxygen species under visible light irradiation. In this way, strong light-induced self-diffusiophoretic effect is achieved, resulting in good dispersion of COFs. Among them, COF-909-Fe showed the highest dispersion performance, along with a drastic decrease in particle size from 5 μm to 500 nm, within only 30 min light irradiation, which is inaccessible by using traditional magnetic stirring or ultrasonication methods. More importantly, benefiting from the outstanding dispersion efficiency, COF-909-Fe micro/nanomotors were demonstrated to be efficient in photocatalytic degradation of tetracycline, about 8 times faster than using traditional magnetic stirring method. This work opens up a new avenue to prepare isolated nanosized COFs in a high-fast, simple, and green manner.

Keywords: Micro/nanomotor; COFs; Exfoliation; Nanocatalyst; Photocatalysis

1. Introduction

The field of micro/nanomotors has progressed significantly with various artificial structures designed over the past decade [1–5]. Among the numerous approaches to drive micro/nanomotors such as chemical [6–8], electric [9,10], magnetic [11,12] and acoustic fields [13], light-driven micro/nanomotors have attracted great attention, since they can be remotely controlled by diverse light signals [14–18]. Especially, as a renewable and abundant energy, visible light has shown its advantage in facile wireless remote control of micro/nanomotors with zero wastes [19,20]. Light-driven micro/nanomotors were generally constructed by incorporating photactive materials, including photocatalysts, photothermal, and photochromatic materials, into their structures [2,21]. Several breakthroughs

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towards practical applications of those motors have been attained, mainly in the fields of environmental and biomedical applications where a large number of tiny motors were used [22–26]. In these applications, the collective behaviors of micro/nanomotors are important to function cooperatively in a smart way [27], as well as the porosity of the motor chassis, which are the basic requirements for cargo loading, transport and release, such as drugs and pollutants [26,28].

As a typical class of crystalline porous materials, covalent organic frameworks (COFs) represent a fast-developing branch in material science, owing to their high porosity and easy functionality nature [29–33]. They have shown great potential applications as storage media for gases, drugs, scaffold for catalysis and photocatalysts for hydrogen generation, CO2 reduction and degradation of organic contaminants [34–38]. However, most of the COFs, especially two-dimensional (2D) COFs, are often synthesized in an aggregated bulk manner, due to the presence of strong interlayer interactions. Such aggregation behavior, however, seriously restricts their further applications [39–47]. Many strategies have been developed to prepare nano-sized COFs, e.g., magnetic stirring, high-energy ultrasonication exfoliation [41,42], interface growth [43], polymer-assisted solvothermal method [44,45], and the substrate-assisted growth method [46,47]. However, most of these strategies exhibit disadvantages, such as time-consuming, pore damaging, leaching and necessitating strict synthetic conditions.

Herein, for the first time, a visible light-induced, efficient strategy was used to disperse micron-sized COFs aggregates into isolated COFs nanoparticles. It was proved that the metal ions decorated in the COF-909 backbone not only promote the electron–hole separation but also serve as a Fenton agent to trigger the production of sufficient reactive oxygen species under visible-light irradiation. The asymmetric distribution of ionic and nonionic species around an irregular shaped COF particle induces a diverging flow and the self-diffusiophoretic propulsion. Moreover, the diverging flow generated by COF-909-Fe motors is demonstrated to be efficient in both generating reversible expansion/contraction microfireworks under pulsed visible light and exfoliating the fused COF-909-Fe particles. The comparison with traditional dispersion methods such as magnetic stirring and ultrasonication demonstrated the high efficiency of the diffusio-phoretic flow method, where nanosized COFs with a narrow size distribution were obtained. Additionally, COF-909-Fe displayed excellent performance in photocatalytic degradation of tetracycline, of which the kinetic reaction rate is ca. 8 times higher than that using traditional magnetic stirring method, as well as a good stability. The photocatalytic efficiency of COF-909-Fe motors is accelerated by the nano catalysts with an enhanced diffusion which improves the interaction between active sites and the pollutant.

2. Experimental section

2.1. Chemicals and materials

Hydrogen peroxide (H2O2, 30 wt%), tetracycline (TC), dimethyl terephthalate and anhydrous MeOH were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Ferric chloride (FeCl3) was bought from Sigma–Aldrich and used as received. Ultra-pure water (18.25 MΩ, Milli-Q Millipore) was used in all experiments. All chemical reagents were analytic grade and used without further purifications.

2.2. Preparation of COF-909-Fe rods

COF-909 was prepared as reported previously (see details in supplementary materials) [38]. For the preparation of COF-909-Fe, 100 mg of FeCl3 was dissolved in 10 mL of anhydrous methanol, followed by adding 20 mg of COF-909. After stirred for ca. 8 min, the yellowish COF-909 particles became dark brown. Upon 12 h, the formed COF-909-Fe was repeatedly washed with 10 mL of anhydrous methanol for three times, immersed in anhydrous methanol for 3 days during which the solution was refreshed every 9 h, and finally dried under vacuum at 100 °C for 12 h.

2.3. Characterization of COF-909 and COF-909-Fe

The crystalline structures of COF-909 and COF-909-Fe were detected by powder X-ray diffraction (XRD, Rigaku Smartlab-SE) using Cu Kα lines focused radiation at 9 kW (45 kV, 200 mA) in the range of 2°–30°. The morphology was studied by field-emission scanning electron microscopy (SEM, SU8010). Transmission electron microscope (TEM) images were collected by using JEOL 2100F microscope and Tecnai G2 F30. A weighted amount of COF-909-Fe was stored at 100 °C for 12 h in a vacuum oven prior to N2 adsorption/desorption measurements using Micromeritics ASAP 2460 at 77 K. The specific surface area was calculated by using Brunauer-Emmett-Teller (BET) model. X-ray photoelectron spectroscopy (XPS) was measured using a spectrometer (Thermo ESCALAB 250XI). The zeta potentials of COF-909 and COF-909-Fe were measured in deionized water on a Zetasizer (Nano ZS, Malvern). Fourier-transformation infrared spectroscopy (FTIR) spectra were measured on a Thermo Scientific Nicolet 6700. The photocurrent measurement and electrochemical impedance spectroscopy (EIS) were executed on a CHI660E electrochemical workstation (CH Instruments, Inc.). A standard three-electrode system was used for the measurement, i.e., a Pt foil as the counter electrode and Ag/AgCl as the reference electrode. The working electrode was prepared as following: 10 mg of sample was dispersed in 1 mL ultrapure water/ethanol mixture, followed by adding 50 μL of Nafion. After ultrasonication for 30 min, 150 μL of the uniform mixture was dropped onto an ITO glass, and dried at room temperature. The effective testing area of the working...
electrode is $1 \times 0.8 \text{ cm}^2$. The solid-state nuclear magnetic resonance (NMR) measurement was carried out using a Bruker AVANCE III HD 400 MHz spectrometer. Sample was packed in rotors at ambient conditions and the spectrum was taken at room temperature. The chemical shifts for $^{13}$C spectrum were referenced to the signal from the carbon of the deuterated solvent. Thermogravimetric analyses (TGA) were carried out on a TA-TGA 55 thermal analyzer. The experiments were performed under dynamic mode and air atmosphere with the flow rate of 60 mL min$^{-1}$. Each sample was heated from room temperature to 800 °C at 10 °C min$^{-1}$.

2.4. Motion characterization of COF-909-Fe motors

Typically, 400 µL of 0.5–2 wt% H$_2$O$_2$ solution was dropped into the sample cell constructed by a poly (methyl methacrylate) ring with an inner diameter of 20 mm and a height of 1 mm adhered on the glass slide by a two-component epoxy glue (Scotch-Weld, 3M, China). A small amount of COF-909-Fe powder was added into the solution followed by immediately covering with a cover glass to avoid contamination with dust. The sample cell was loaded on an upright optical microscope (Axioscope 5, Carl Zeiss, Germany) connected with a CCD camera. Due to gravity, particles mostly settled to the bottom of the sample cell, and videos were recorded at this plane with a frame rate of 30 fps. However, when irradiated with visible light from a Halogen Cold light source connected with two optical fibers (MLED500, Dayueweijia, China), the particles especially small ones, could float upward (diffusophoresis discussed in the main text). The light intensity that shot onto the sample was measured by a CEL-FZ-A optical power meter (300–1100 nm, Ceaulight, China) and adjusted in the range of 100–300 mW cm$^{-2}$. The transmission light source from the microscope has an intensity of 0.05–3 mW cm$^{-2}$, recorded as “dark” condition.

Videos were analyzed with Tracker 4.9x software. From the trajectory of particles, the mean square displacement (MSD) and the effective diffusion coefficient ($D_e$) were calculated and averaged over ten particles.

2.5. Collective behaviors of COF-909-Fe motors

The collective behaviors of COF-909-Fe motors were characterized under 300 mW cm$^{-2}$ visible light illumination in a 0.5 wt% H$_2$O$_2$ solution. Videos were taken while the visible light was repeatedly switched on and off at set time intervals. The average particle distance was measured by tracking the positions of all particles in each frame. Tracer particles (SiO$_2$ particles with a diameter of 1.0 µm, Sigma–Aldrich) were used to detect the flow generated by COF-909-Fe motors. The behavior of COF-909-Fe motors under continuous light irradiation was observed in a culture dish (diameter = 20 mm) and videos were recorded by a digital camera.

2.6. Dispersion of COF-909-Fe in aqueous solution

We compared the dispersibility of COF-909-Fe by visible-light induced self-propulsion with the other two commonly used dispersing methods, i.e., ultrasonication and magnetic stirring. For ultrasonication and magnetic stirring, 1 mg COF-909-Fe was added into 20 mL deionized water, and then the suspension was subjected to ultrasonication or magnetic stirring under dark condition for different time. For visible-light induced self-propulsion, 1 mg COF-909-Fe was added into 20 mL 0.5 wt% H$_2$O$_2$ solution, and then the suspension was irradiated under 300 mW cm$^{-2}$ visible light. At set time intervals, 0.5 mL solution was taken out and observed under an optical microscope with a 50× objective. Images were captured at different positions of the sample and analyzed using ImageJ software to get statistics on particle sizes over 1200 particles. When the size of COF-909-Fe particles is smaller than 1 µm, dynamic light scattering (Nano ZS 90, Malvern) was used to measure the average particle size and size distribution. The morphology of particles after 2 h of treatments was further observed by SEM.

2.7. Adsorption and degradation of tetracycline (TC)

The catalytic performance of COF-909-Fe motors was assessed by the degradation of TC, a model toxic organic compound, in a 30 mL vial at 25 °C. Firstly, 1 mg COF-909-Fe was put into 20 mL TC aqueous solution (30 mg L$^{-1}$) with 0–2 wt% H$_2$O$_2$. The suspension was stored in dark for 30 min to attain the adsorption–desorption equilibrium before initiating the photocatalytic experiment. In the presence of H$_2$O$_2$, Fenton-like reaction happened in dark condition. At the designed intervals, 0.6 mL suspension was taken out and filtered with a poly (vinylidene fluoride) membrane to get rid of COF-909-Fe. The concentration of TC was quantitatively monitored by an Ultimate 3000 UHPLC-Q Exactive liquid chromatograph/mass spectrometer (LC/MS, Thermo Scientific, US) using a Hypersil GOLD column and a HESI source in positive ion mode.

2.8. Adsorption and degradation of dimethyl terephthalate (DMT)

Typically, 1 mg COF-909-Fe was added into 20 mL DMT aqueous solution (30 mg L$^{-1}$) with/without 0.2 wt% H$_2$O$_2$. The suspension was placed in dark condition for 30 min before irradiation under 300 mW cm$^{-2}$ visible light. Degradation of pure DMT solution under visible light was also investigated. At the given intervals, 0.5 mL suspension was taken out, filtered with poly (vinylidene fluoride) membrane (pore size of 0.22 µm) and measured by a high performance liquid chromatography (HPLC, LC-100, Shanghai Wufeng Scientific Instrument Co. Ltd., China), which consisted of a Shodex C18
column (250 × 4.6 mm, 5 μm). The mobile phase contained 50% methanol (HPLC-grade) and 50% formic acid solution (formic acid 0.2%). The flow rate was 1 mL min⁻¹ and the detection wavelength was set at 252 nm.

3. Results and discussion

3.1. Morphology and structure of COF-909-Fe

COF-909-Fe nanorods were synthesized at the basis of high-efficiency coordinative bonding between terpyridyl of COF-909 and iron ions (Scheme 1 and Fig. 1a). As shown in the powder XRD patterns (Fig. 1b and S1), COF-909-Fe possesses an analogous crystal structure with COF-909. The peaks at 3.3°, 4.2°, 5.4°, 6.7° and 25.8° in the XRD pattern of COF-909-Fe correspond to the (hkl) values of (110), (200), (020), (220) and (001), respectively. Consistently, an interlayer spacing of 0.36 nm is observed in the high-resolution TEM image (Fig. 1c). SEM and TEM images (Fig. 1d and S2) show the morphology of COF-909-Fe. COF-909-Fe has a clear nanorod shape with the length of 100–450 nm and the width of 44.5 ± 5.9 nm, which is analogous to those of COF-909 (Fig. S3). Due to the strong interlayer π–π interaction and low solubility of COF-909 in solution, the strong agglomeration tendency during synthesis leads to the formation of irregular shaped particles with sizes varying from 2.9 μm to 6.3 μm. Moreover, the as-prepared COF-909-Fe represents a porous framework with BET surface area of 500 m² g⁻¹, much lower than that of COF-909 (2600 m² g⁻¹), owing to the coordination of Fe within the multilinker [38] (Fig. 1e). The pore size of COF-909-Fe calculated by quenched solid density functional theory (DFT) is slightly smaller than that of COF-909, due to the coordination of Fe within the multiple N-linker (Fig. 1f).

The chemical composition and elemental valence state of COF-909-Fe were characterized by XPS (Fig. 1g–i), confirming the existence of C, O, N and Fe in COF-909-Fe. The content of Fe in COF-909-Fe is ca. 7.8 wt% (Fig. 1g and Table S1), higher than that reported in previous literature [48], suggesting the good coordination of iron and terpyridyl. Thermogravimetric analysis results confirm the content of Fe (Fig. S4). High-resolution Fe 2p XPS spectrum of COF-909-Fe was deconvoluted into four peaks. The peaks at 710.0 and 723.4 eV are allotted to Fe 2p₃/₂ and Fe 2p₁/₂ orbitals, respectively, demonstrating the existence of Fe(II) due to the coordination effect of Fe with COF-909 [48,49]. The peaks at 713.7 and 728.9 eV correspond to Fe(III) in COF-909-Fe (Fig. 1f) [48,50,51]. In high-resolution N 1s XPS spectrum, a new peak at 398.6 eV indicates the coordination of Fe, whilst the pyridinic N induces the main peak at 399.5 eV (Fig. 1g). Furthermore, the structure of COF-909 and COF-909-Fe was characterized by ¹³C NMR spectroscopy and FTIR (Fig. S5). In the ¹³C NMR spectrum, the characteristic signal of imine bond is observed at 156.2 ppm, indicating the successful synthesis of COF-909. FTIR curve exhibits two characteristic peaks at 1433 and 1605 cm⁻¹, ascribed to ν (-C=N-) in pyridine ring and imine bond, respectively.

3.2. Electrochemical properties of COF-909-Fe

In UV-Vis diffuse reflectance spectra, COF-909-Fe shows a strong light absorption in the wavelength range of 400–750 nm, much stronger than that of COF-909 (Fig. 2a), originating from the ligand-filed charge transfer [47,52]. The valence band and band gap of COF-909-Fe are 0.91 and 1.59 eV, respectively (Fig. 2b and S6). The narrower band gap between frontier orbitals helps the excitation of COF-909-Fe by visible light, compared to COF-909 [53]. The photo-induced charge transfer and separation behavior of COF-909 and COF-909-Fe was measured by transient electrochemical spectroscopy (EIS). Nyquist plot of COF-909-Fe exhibits a smaller arc radius (Fig. 2d), indicating the higher efficiency of charge transfer and separation.

3.3. Self-propulsion of COF-909-Fe

When dispersed in a low concentration (0.5–2 wt%) H₂O₂ solution and irradiated by visible light, COF-909-Fe particles perform active Brownian motion in aqueous solution (Fig. 3a and Video 1). Longer trajectories are observed with the increase of H₂O₂ concentration and/or light intensity during the same time interval, indicating the effectiveness of fuel introduction and energy input. Note that, regardless of the fuel concentration and light intensity, the trajectories are not straight, due to rotational motions induced by thermal fluctuations [54]. The motion of COF-909-Fe motors was further...
quantified by calculating the mean square displacement (MSD) and the corresponding effective diffusion coefficient ($D_e$) by fitting the linear region of MSDs to Eq. (1):

$$D_e = \frac{\text{MSD}}{4\Delta t}$$

The MSD curves of COF-909-Fe show linear and parabolic dependence on time intervals ($\Delta t$) for non-activated and active states (Fig. 3b and c and Fig. S7a). The $D_e$ value of the passive Brownian motion in water is ca. 0.03 $\mu$m$^2$ s$^{-1}$. By contrast, without visible light irradiation, the value of $D_e$ only increases to 0.2 $\mu$m$^2$ s$^{-1}$ and 0.3 $\mu$m$^2$ s$^{-1}$, respectively, as the H$_2$O$_2$ concentration is raised to 0.5 and 2 wt% (Fig. S7b). When the H$_2$O$_2$ concentration keeps at 0.5 wt% and the visible light of intensity goes up from 0 to 100 and 300 mW cm$^{-2}$, the value of $D_e$ increases to 0.2, 0.3 and 1.1 $\mu$m$^2$ s$^{-1}$, respectively (Fig. 3d). At visible light intensity of 300 mW cm$^{-2}$, $D_e$ increases from 0.08 $\mu$m$^2$ s$^{-1}$ to 1.2 $\mu$m$^2$ s$^{-1}$ and 2.5 $\mu$m$^2$ s$^{-1}$, respectively, when the H$_2$O$_2$ concentration changes from 0 wt% to 0.5 wt% and 2 wt% (Fig. 3e). In addition, the self-propelling COF-909-Fe particles are accompanied by a diverging flow as characterized by silica tracer particles of diameter 1.0 $\mu$m (Fig. 3f).

The active motion of COF-909-Fe is related to two main reactions (Fig. 4a), including (1) Fenton-like reaction between coordinated iron ions and hydrogen peroxide without light as shown in Eqs. (2) and (3):

$$\text{Fe(II)} \rightarrow \text{Fe(III)} + \cdot \text{OH} + \cdot \text{OH}^- \quad (2)$$

$$\text{Fe(III)} \rightarrow \text{Fe(II)} + \cdot \text{H} + \cdot \text{O}_2^- \quad (3)$$

and (2) light-triggered electron–hole separation of COF-909-Fe when irradiated by photons of energy equal to/higher than its bandgap resulting in the redox reactions of hydrogen peroxide, as shown in Eqs. (4)–(7):

$$\text{COF} \rightarrow \text{COF} + \cdot \text{H} + \cdot \text{e}^- \quad (4)$$

$$\text{H}_2\text{O}_2 + \cdot \text{H} \rightarrow \text{O}_2 + \cdot \text{H}_2\text{O} \quad (5)$$

$$\text{H}_2\text{O}_2 + \cdot \text{e}^- \rightarrow \text{O}_2^- + \cdot \text{H}_2\text{O} \quad (6)$$

$$\text{H}_2\text{O}_2 + \cdot \text{e}^- \rightarrow \cdot \text{O} + \cdot \text{H} + \cdot \text{OH}^- \quad (7)$$

Furthermore, under visible light irradiation, Fenton-like reaction is accelerated, as the produced electrons on the surface...
of COF-909-Fe enhance the transition from Fe(III) to Fe(II). Due to the different diffusivity of the released ionic species, local converging or diverging diffusioelectric ($E$-) fields are established [55]. These $E$-fields act on the positively charged surface of COF-909-Fe (zeta potential = $(33.9 \pm 3.8)$ mV), inducing a diverging flow (Fig. 3f). Similar but weaker $E$-fields induce a converging flow on the negatively charged surface of COF-909 (zeta potential = $(-14.7 \pm 5.5)$ mV) (Fig. S8 and Video 2). The contribution of surface electro-osmotic flow is minor, otherwise similar flows should be observed in both cases. The asymmetric distribution of ionic and reactive oxygen species (ROS) around COF-909-Fe due to its irregular shape...
Fig. 4. Scheme for the self-propulsion mechanism of COF-909-Fe motors.

Fig. 5. Collective behaviors of COF-909-Fe micromotors in 0.5 wt% H₂O₂ solution under 300 mW cm⁻² visible light irradiation. (a) The COF-909-Fe particles repel each other when visible light is turned on and (b) reaggregate when light is tuned off. The scale bar in (b) applies for all the images in (a) and (b). (c) Time variation of the average center-to-center distance of neighboring COF-909-Fe particles during the process of light on (color shaded region) and off within three cycles. (d) Distribution of the exclusion distance measured from the surface of COF-909-Fe motor in 0.5 wt% H₂O₂ solution at 300 mW cm⁻² visible light irradiation.
breaks the symmetry of flow and \( E \)-fields, yielding the self-diffusiophoretic propulsion (Fig. 4b) [55].

### 3.4. Collective behaviors of COF-909-Fe motors

COF-909-Fe particles have a strong tendency to aggregate in aqueous solution due to the hydrophobicity. Upon exposure to visible light (e.g., 300 mW cm\(^{-2}\)) in a low concentration \( \text{H}_2\text{O}_2 \) solution, the diverging flow generated by COF-909-Fe motors acts as repulsion force pushing neighboring particles away, leading to the expansion of the group (Fig. 5a and Video 3). The average interparticle center-to-center distance also increases with irradiation time, reaching an average value of 8.7 \( \mu \)m within 1 min. When visible light is turned off, COF-909-Fe particles slowly diffuse to the aggregated state (Fig. 5b). This expansion-contraction process can repeat for several times (Fig. 5c) before big ones are split into small ones and leave the group. Consistently, a single COF-909-Fe motor produces an exclusion zone of ca. 6.7 \( \mu \)m where tracer particles are swept out (Fig. 5d).

### 3.5. Dispersion of COF-909-Fe in aqueous solution

Fig. 6a–d depicts the collective behaviors of COF-909-Fe motors under continuous light irradiation in macroscale. The macroscale crowd of COF-909-Fe particles shows a similar expansion with the microscale group and disperses into 0.5 wt% \( \text{H}_2\text{O}_2 \) aqueous solution within 25 min at 300 mW cm\(^{-2}\) visible light irradiation. This expansion is promoted by the generated diverging flow and the perturbation from \( \text{O}_2 \) bubbles (Video 4). Photothermal effect is ruled out for the dispersion of COF-909-Fe since no obvious temperature gradient is observed during the experiment (Fig. S9). More importantly, the diverging flow that propels the motor also causes the exfoliation of COF-909-Fe aggregates into nanoparticles (Fig. 6g–i). Statistical analysis on images of more than 1200 particles shows that the average particle size decreases from ca. 4.3 \( \mu \)m to 770 nm within 30 min (Fig. S10). Dynamic light scattering was further used to characterize the size of particles smaller than 1 \( \mu \)m (Fig. S11). The submicron sized particles were continuously exfoliated to form nanoparticles of a few hundred nanometers within 2 h (Fig. 6i). Complementary SEM images present rod-like nanoparticles with the length of 353.5 ± 129.2 nm and the width of 133.2 ± 26 nm (Fig. 6g and h and S12). Powder XRD patterns of these nanoparticles show similar (110), (200), (020), (220) peaks and an almost diminished (001) peak compared with the bulk material, indicating an exfoliated COF-909-Fe with a retained interplanar structure (Fig. S13). For comparison, conventional dispersion methods such as magnetic stirring and ultrasonication were used to disperse COF-909-Fe particles in deionized water. After 2 h, the as-prepared particles show a broad size distribution with an average size of ca. 2.2 \( \mu \)m (Fig. 6i and S10). After being treated by the same visible light and fuel, the average size of COF-909 changes from 16.6 \( \mu \)m to 8.3 \( \mu \)m (Fig. S14), implying that the converging flow generated by COF-909 particles does not help the exfoliation.

![Fig. 6. Dispersion of COF-909-Fe in aqueous solution. (a–d) Representative collective behavior of a crowd of COF-909-Fe particles in 0.5 wt% \( \text{H}_2\text{O}_2 \) aqueous solution under continuous visible light irradiation of 300 mW cm\(^{-2}\) (L300). The crowd expands in size and slowly diminishes within 25 min. The scale bar in (d) applies for (a)–(d). Insets show schemes of the microscopic behaviors of COF-909-Fe motors. SEM images of COF-909-Fe particles dispersed in aqueous solution via (e) magnetic stirring, (f) ultrasonication, and (g and h) light-triggered self-propulsion in 0.5 wt% \( \text{H}_2\text{O}_2 \) solution at 300 mW cm\(^{-2}\) light for 1.5 h. (i) Time variation of the average particle size using three different dispersion methods.](image-url)
Fig. 7. Absorption spectra of processed TC solution obtained at different time using (a and b) magnetic stirring under 100 mW cm$^{-2}$ (denoted L100) and 300 mW cm$^{-2}$ (denoted L300) visible light without H$_2$O$_2$ as control experiments, and (c and d) self-propulsion in 0.5 wt% H$_2$O$_2$ under L100 and L300.

Fig. 8. Concentration ratio $C/C_0$ of TC as a function of time for the processing (a) without and (b) with H$_2$O$_2$. (c) Pseudo-first-order kinetic constants ($k$) of TC degradation using different systems. (d) Comparison of COF-909-Fe and up-to-date photocatalysts in the degradation efficiency of TC (Table S1).
3.6. Photocatalytic performance of COF-909-Fe motors

The dispersion of COF-909-Fe particles from microscale to nanoscale by light-triggered self-propulsion endows COF-909-Fe nanomotors with a large specific surface area, which could effectively promote their photocatalytic performance. The photocatalytic activity of COF-909-Fe motors is assessed by the degradation of TC, a model poisonous contaminant, under visible-light irradiation (Figs. 7 and 8 and S15). As a typical antibiotic, TC is commonly used in medicine to treat microorganism infections in human and veterinary. Thereby, it is of great importance for the degradation of TC prior to the release into the environment [50,56–59]. Notably, TC is stable to visible light and does not show obvious degradation under 300 mW cm\(^{-2}\) irradiation (Fig. S16). Without light irradiation, Fenton-like reaction alone has a degradation efficiency of ca. 33% (Fig. S17). For comparison, the characteristic peak of TC in UV-Vis spectra at 357 nm lowers down with time under magnetic stirring (Fig. 7a and b). The degradation efficiency increases from 26.7% to 46.2% and 77.5% within 2 h, as the visible-light intensity is increased from 0 mW cm\(^{-2}\) to 100 mW cm\(^{-2}\) and 300 mW cm\(^{-2}\) (Fig. 8a). By contrast, the characteristic peak almost diminishes within 2 h for COF-909-Fe motors in 0.5 wt% \(\text{H}_2\text{O}_2\) solution under 100 mW cm\(^{-2}\) visible light (Figs. 7c and 8b). As the light intensity is increased to 300 mW cm\(^{-2}\), the characteristic peak of TC diminishes within 90 min (Figs. 7d and 8b).

The photocatalytic degradation kinetics of TC obeys the pseudo-first order, i.e., \(\ln \left(\frac{C}{C_0}\right) = -kt\), where \(k\) is the kinetic constant (Fig. S15). The kinetic constants of COF-909-Fe motors at 100 and 300 mW cm\(^{-2}\) visible light are ca. 0.036 and 0.020 min\(^{-1}\), respectively, which are 7.6 and 3.5 times higher than that of COF-909-Fe under magnetic stirring and the same light irradiation (Fig. 8c). Moreover, the COF-909-Fe motors outperform the up-to-date catalysts, in the degradation rate of TC [56–59] (Fig. 8d and Table S2). Furthermore, a colorless pollutant, namely dimethyl phthalate, with an initial concentration of 30 ppm, was used to evaluate the photocatalytic activity of COF-909-Fe motors. Within 10 min, COF-909-Fe motors degrade ca. 99% of the dimethyl phthalate, indicating their good photocatalytic activity (Fig. S18).

The photocatalytic stability of COF-909-Fe motors was further examined. High-speed centrifugation was used to reclaim the nanomotors from the solution, followed by repeatedly washing with deionized water before re-dispersed into TC-polluted water. After 5 cycles, the removal efficiency of TC retains above 94% (Fig. 9), exhibiting the good recyclability of COF-909-Fe motors. In practical application, COF-909-Fe could be loaded onto a scaffold to solve the separation problem.

TC can be effectively degraded by the produced ROS, including \(\text{O}_2\)• and •OH into intermediate products (Fig. S19), leading to a color change from light yellow to colorless (Video 5). Nine main intermediates are detected (Fig. S20), and the proposed degradation pathway of TC is shown in Fig. 10. Most of the intermediates are mineralized into carbon dioxide, water and other low molecular weight products.

The catalytic enhancement of COF-909-Fe motors mainly results from four aspects as follows: Firstly, the separation of electrons and holes as well as the production of ROS on the surface of COF-909-Fe are effectively promoted by light irradiation. Secondly, the formed \(\text{O}_2\) bubbles from the

![Fig. 10. Proposed pathways of TC degradation by COF-909-Fe motors under visible light.](image-url)
decomposition and/or oxidation of H$_2$O$_2$ under visible-light irradiation introduce random perturbations to enhance the mass change by generating active convection (Video 5). Thirdly, self-diffusiophoresis induces exfoliation of COF-909-Fe into nano-catalysts. The nano-catalysts thus provide more specific contact areas and active sites to interact with TC molecules. Fourthly, the random self-propulsion of COF-909-Fe micro/nanomotors could effectively perturb the suspension. Meanwhile, as COF-909-Fe gets smaller, the gravity induced sedimentation becomes weaker, and more COF-909-Fe nanomotors can randomly explore larger three-dimensional space, favoring for the improvement of photocatalytic activity.

4. Conclusion

In summary, we report the self-propulsion induced exfoliation of COF-909-Fe motors to fabricate nanoscale catalysts, which show greatly enhanced photocatalytic performance in a physiologically low (0.5 wt%) H$_2$O$_2$ solution under visible light irradiation. The asymmetrical distribution of ionic and ROS species around the COF-909-Fe particle induces a diverging flow and self-diffusiophoretic propulsion. These motors show reversible microfireworks when light is alternately turned on and off. More importantly, the diverging flow effectively overcomes the interlayer π-π stacking and exfoliates the microparticles into nanoscale. These nanomotors exhibit high degradation efficiency of TC, facilitated by the random self-propulsion, O$_2$ bubble generated active convection, as well as good photocatalytic stability. The self-propulsion induced exfoliation of COF materials shows promise for the environmental and biomedical applications such as catalysis, chemical sensing, and intravenous injection, where nanoparticles are required.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gee.2021.09.002.

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