Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
Recoverable peroxidase-like Fe₃O₄@MoS₂-Ag nanozyme with enhanced antibacterial ability

Feng Wei, Xinyu Cui, Zhao Wang, Changchang Dong, Jiadong Li, Xiaojun Han *

State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Keywords:
Antibacterial activity
Nanozyme
Peroxidase-like activity
Bacteria-binding
Photothermal effect

ABSTRACT

Antibacterial agents with enzyme-like properties and bacteria-binding ability have provided an alternative method to efficiently disinfect drug-resistance microorganism. Herein, a Fe₃O₄@MoS₂-Ag nanozyme with defect-rich rough surface was constructed by a simple hydrothermal method and in-situ photodeposition of Ag nanoparticles. The nanozyme exhibited good antibacterial performance against E. coli (~69.4%) by the generated ROS and released Ag⁺, while the nanozyme could further achieve an excellent synergistic disinfection (~100%) by combining with the near-infrared photothermal property of Fe₃O₄@MoS₂-Ag. The antibacterial mechanism study showed that the antibacterial process was determined by the collaborative work of peroxidase-like activity, photothermal effect and leakage of Ag⁺. The defect-rich rough surface of MoS₂ layers facilitated the capture of bacteria, which enhanced the accurate and rapid attack of “OH and Ag⁺” to the membrane of E. coli with the assistance of local hyperthermia. This method showed broad-spectrum antibacterial performance against Gram-negative bacteria, Gram-positive bacteria, drug-resistant bacteria and fungal bacteria. Meanwhile, the magnetism of Fe₃O₄ was used to recycle the nanozyme. This work showed great potential of engineered nanozymes for efficient disinfection treatment.

1. Introduction

The increase of drug-resistant microorganism, caused by over usage of antibiotics, has become a serious public threat to human [1,2]. Therefore, enormous attention has been paid to urgent developing various antibacterial agents with broad-spectrum antimicrobial property and minor side effect [3]. As with the development of nanotechnology, noble metals, especially Ag nanoparticles, have been widely applied due to their potent antibacterial properties [4,5]. Nevertheless, the effective application has been limited by the easy aggregation of small nanoparticles, which requires suitable matrix for accurate design of the nanoparticle loading. Moreover, the excessive leakage of metal ions can inevitably result in the toxicity to the organism [6]. To avoid the above issues, considerable efforts have been dedicated in alternative strategies without detrimental effects [7]. Recently, the property of natural enzymes to produce reactive oxygen species (ROS) has been used in disinfecting microorganism [8]. Unfortunately, the natural enzyme always suffers from high cost and environment-dependence [9,10]. The further attraction has been focused on the construction of artificial nanozymes which endow stable materials with promising ROS production features [11]. Some inorganic materials, such as ferroferric oxide [12], graphene quantum dots [13] and cerium dioxide [14], have shown strong intrinsic peroxidase-like properties, which can mimic enzymes and effectively catalyze a low concentration of H₂O₂ into highly active •OH [15]. These nanozymes exhibited excellent antibacterial activity in disinfection treatment using •OH to destroy the membranes of bacteria via oxidization [16]. However, the effective bacteriotoxic application of nanozymes still needs extensive improvement in many aspects [17]. For instance, the low bacteria-binding ability of most artificial enzymes as well as the short lifetime and poor diffusivity of ROS greatly hindered their interaction with bacteria and limited the disinfection performance. Hence, it is still a great challenge to develop creative strategies to address the aforementioned issues and limitations.

During the disinfection process, the interaction between bacteria and antibacterial agents is well recognized to be one of the necessary steps to determine the disinfection performance [18,19]. In this regard, the adhesive ability of the antibacterial agents plays a significant role in effective capture and exact attack process. Inspired by the natural trapping system, the rough material surface with protuberance or pili,
such as pollen [20], spike on the coronaviruses and flagella of the bacteria, exhibits better adhesion towards the substrate compared to the flat surface. Studies have also shown that the promoted adhesive ability of nanomaterials mainly originates from regulating the topological structures on the surface to increase the roughness [21,22]. Lately, remarkable works have been done by fabricating defect-rich 2D-layers MoS₂ on the surface of Cu nanowires to develop a multifunctional artificial nanozyme with good capture ability to integrate the advantages of single component [23]. As a typical material of transition metal dichalcogenides (TMDs), MoS₂ possesses 2D-layer structure with huge specific surface area, facile surface modification and good biocompatibility, making it a proper candidate as well as a supportive matrix for other material attachment [24] in the fields of catalysis [25], energy storage [26] and hydrogen evolution [27]. The excellent absorption in near-infrared range and the friendly elements of Mo and S to human body enable it accessible in photothermal therapy (PTT) [28], which can also be applied in disinfection treatment as a noninvasive method [29-31]. Meanwhile, the peroxidase (POD)-like property of MoS₂ was explored in the colorimetric detection of H₂O₂ and glucose [32], which is rarely reported in antibacterial treatment. Therefore, the smart engineered nanozymes by combination of PTT and peroxidase-like properties can provide an intriguing alternative for disinfection treatment.

The recent reported literatures have combined different bactericidal modalities (such as metal ions, ROS, hyperthermia) to achieve the synergic effect with decreased dose of antibacterial agents and increased efficiency. However, the long distance between antibacterial agents and bacteria still limited their interaction and negatively influenced the disinfection efficiency. To solve the aforementioned issues, herein, a Fe₃O₄@MoS₂-Ag with rough surface was constructed by a simple hydrothermal method and in-situ photodeposition of Ag nanoparticles as shown in Scheme 1. It was found that the surface topologies of Fe₃O₄ nanoparticles were modified by defect-rich MoS₂ layers vertically growing on the surface, which showed excellent bacteria-binding ability. Notably, the combination of Fe₃O₄ and MoS₂ further enhanced the intrinsic peroxidase-like properties. Moreover, the hyperthermia by the photothermal property of Fe₃O₄@MoS₂-Ag assisted to prohibit the bacterial growth. The magnetism of Fe₃O₄ enable the nanozyme to be easily recycled. The advantages were: i) the intrinsic POD-like property of Fe₃O₄@MoS₂-Ag could catalyze a low concentration of H₂O₂ into toxic •OH, which showed a great potential in inflammation treatment; ii) the released Ag⁺ played an auxiliary role to attack the bacterial membranes; iii) the photothermal effect of Fe₃O₄@MoS₂-Ag not only generated hyperthermia but also improved the POD-like property; iv) the topological structure and S-vacancy of MoS₂ nanosheets endowed Fe₃O₄@MoS₂-Ag with potent adhesion ability to bacteria by forming chemical bonds, which shortened the diffusion distance of short-life •OH radicals and further enhanced the antibacterial effect. Therefore, this work provided a promising strategy for rapid and effective disinfection treatment and showed great potentials in practical inflammation treatment.

2. Material and methods

2.1. Materials

Iron (III) chloride hexahydrate (FeCl₃·6H₂O), sodium acetate (NaAc) and ethylene glycol (EG) were purchased from Tianjin Fuyu Fine Chemical Reagent Corporation. Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), thiourea (CH₄N₂S), polyethylene glycol (PEG 1000), silver nitrate (AgNO₃), glutaraldehyde (2.5%), 3, 3, 5, 5-Tetramethylbenzidine (TMB) and terephthalic acid (TFA) were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). Methanol, hydrogen peroxide (H₂O₂) and dimethyl sulfoxide (DMSO) were provided by Xilong chemicals (China). All chemicals were used without any treatment.

2.2. Preparation of Fe₃O₄@MoS₂-Ag

Firstly, Fe₃O₄ particles were prepared via a solvothermal method in the reported literature with a little modifications [33]. In brief, 1.35 g FeCl₃·6H₂O was dissolved into 40 mL EG with stirring to form a yellow transparent solution, after which 3.6 g NaAc and 1.0 g PEG were added into the solution successively. The mixed solution was stirred vigorously, followed by transference to a 100 mL sealed Teflon-autoclave. The mixture was kept at 200 °C for 8 h. The obtained black sample was thoroughly washed three times with water and ethanol, respectively, and collected by magnetic separation. The final black product was dried in a vacuum oven at 60 °C overnight.

Secondly, Fe₃O₄@MoS₂ was prepared with a typical hydrothermal method according to the literature [34]. Briefly, 20 mg Fe₃O₄ nanoparticles were uniformly dispersed in 30 mL distilled water by strong sonication for 30 min. After that, 1.05 g (NH₄)₆Mo₇O₂₄·4H₂O and 2.28 g thiourea were added into the solution with ultrasonication for another 30 min. The mixture was transferred into a 50 mL sealed Teflon-autoclave and heated at 180 °C for 10 h. The autoclave was cooled down naturally. The as-prepared sample was washed with water and ethanol in succession for 3 times and collected by magnetic separation to remove MoS₂. The black product was dried in the vacuum oven at 60 °C overnight. The MoS₂ was prepared with the same procedure without the addition of Fe₃O₄.

The in-situ loading of Ag was prepared by photo-deposition following our previous method [35]. Specifically, 100 mg Fe₃O₄@MoS₂ powder was fully dispersed in 100 mL methanol by sonication for 20 min. The designed volume (46.7, 93.5, 280.4 and 467.3 μL) corresponded to 0.5, 1, 3 and 5% compared to Fe₃O₄@MoS₂ powder mass of AgNO₃ aqueous solution (0.1 mol/L) was slowly dropped into the suspension with the mechanical stirring for 15 min to electrostatically attract Ag⁺ onto MoS₂ sheets, followed by bubbling N₂ (99.9999%) into the mixture for 30 min to remove O₂. The photo-deposition process was conducted using a 300 W mercury lamp for 3 h. After washing with distilled water for 3 times and collecting by magnetism, the final product was dried in the vacuum oven at 60 °C overnight. The samples with different mass percentage of loading Ag compared to Fe₃O₄@MoS₂ powder were termed as Fe₃O₄@MoS₂-0.5%Ag, Fe₃O₄@MoS₂-1%Ag, Fe₃O₄@MoS₂-3%Ag and Fe₃O₄@MoS₂-5%Ag, respectively.

2.3. Characterizations

X-ray diffraction (XRD) pattern from 10° to 90° was conducted to characterize the crystal structure of the as-prepared samples using
Chemical Engineering Journal 408 (2021) 127240

3

The peroxidase-like activity of different samples was evaluated via the oxidation properties of TMB with and without H2O2. Briefly, the as-prepared samples (final concentration of 50 μg/mL) were prepared in the acetic acid - sodium acetate buffer (pH of 4.0), followed by the addition of H2O2 (final concentration of 1 mmol/L) and TMB solution in DMSO (final concentration of 1 mmol/L) at room temperature. All catalytic activities were monitored by the absorbance change of 652 nm from the oxidation product of TMB. The temperature-dependent and pH-dependent peroxidase-like activities were explored by adjusting the temperature and pH with incubation for 5 min before measurement. The peroxidase-like activity under 808 nm laser irradiation was further investigated on the same mixture composition with UV–Vis absorbance spectra recording every 30 s during 10 min.

The final catalyst concentration for kinetics study was 50 μg/mL. Before catalysis, the aqueous solutions of different samples, H2O2 solution and TMB in DMSO were prepared at the concentrations of 500 μg/mL, 10 mmol/L and 10 mmol/L, respectively. For kinetics study, 100 μL of samples were fully mixed with 700 μL of acetic acid - sodium acetate buffer (pH of 4.0) and 100 μL of TMB. The additional 100 μL of H2O2 solution was added to above mixture to start the catalysis process. The kinetics were investigated using below Michaelis-Menten equation.

\[
V_0 = V_{max} \frac{[S]}{K_m + [S]}
\]

where \( V_0 \) represents the initial velocity, \( V_{max} \) refers to the maximum reaction velocity, and \([S]\) is the concentration of substrate.

2.4. Peroxidase-like activity characterization

The peroxidase-like activity of different samples was evaluated via the oxidation properties of TMB with and without H2O2. Briefly, the as-prepared samples (final concentration of 50 μg/mL) were prepared in the acetic acid - sodium acetate buffer (pH of 4.0), followed by the addition of H2O2 (final concentration of 1 mmol/L) and TMB solution in DMSO (final concentration of 1 mmol/L) at room temperature. All catalytic activities were monitored by the absorbance change of 652 nm from the oxidation product of TMB. The temperature-dependent and pH-dependent peroxidase-like activities were explored by adjusting the temperature and pH with incubation for 5 min before measurement. The peroxidase-like activity under 808 nm laser irradiation was further investigated on the same mixture composition with UV–Vis absorbance spectra recording every 30 s during 10 min.

The final catalyst concentration for kinetics study was 50 μg/mL. Before catalysis, the aqueous solutions of different samples, H2O2 solution and TMB in DMSO were prepared at the concentrations of 500 μg/mL, 10 mmol/L and 10 mmol/L, respectively. For kinetics study, 100 μL of samples were fully mixed with 700 μL of acetic acid - sodium acetate buffer (pH of 4.0) and 100 μL of TMB. The additional 100 μL of H2O2 solution was added to above mixture to start the catalysis process. The kinetics were investigated using below Michaelis-Menten equation.

\[
V_0 = V_{max} \frac{[S]}{K_m + [S]}
\]

where \( V_0 \) represents the initial velocity, \( V_{max} \) refers to the maximum reaction velocity, and \([S]\) is the concentration of substrate.

2.4. Peroxidase-like activity characterization

The peroxidase-like activity of different samples was evaluated via the oxidation properties of TMB with and without H2O2. Briefly, the as-prepared samples (final concentration of 50 μg/mL) were prepared in the acetic acid - sodium acetate buffer (pH of 4.0), followed by the addition of H2O2 (final concentration of 1 mmol/L) and TMB solution in DMSO (final concentration of 1 mmol/L) at room temperature. All catalytic activities were monitored by the absorbance change of 652 nm from the oxidation product of TMB. The temperature-dependent and pH-dependent peroxidase-like activities were explored by adjusting the temperature and pH with incubation for 5 min before measurement. The peroxidase-like activity under 808 nm laser irradiation was further investigated on the same mixture composition with UV–Vis absorbance spectra recording every 30 s during 10 min.

The final catalyst concentration for kinetics study was 50 μg/mL. Before catalysis, the aqueous solutions of different samples, H2O2 solution and TMB in DMSO were prepared at the concentrations of 500 μg/mL, 10 mmol/L and 10 mmol/L, respectively. For kinetics study, 100 μL of samples were fully mixed with 700 μL of acetic acid - sodium acetate buffer (pH of 4.0) and 100 μL of TMB. The additional 100 μL of H2O2 solution was added to above mixture to start the catalysis process. The kinetics were investigated using below Michaelis-Menten equation.

\[
V_0 = V_{max} \frac{[S]}{K_m + [S]}
\]

where \( V_0 \) represents the initial velocity, \( V_{max} \) refers to the maximum reaction velocity, and \([S]\) is the concentration of substrate.

2.5. Detection of ‘OH

The production of ‘OH was assessed by the reaction between TPA and ‘OH to produce 2- hydroxyl terephthalic acid, which was monitored by PL with the excitation wavelength at 315 nm and emission wavelength at 435 nm. All mixtures were incubated in PBS (pH of 7.4) at room temperature for 6 h with TPA (0.5 mmol/L), H2O2 (1 mmol/L) and as-prepared samples (100 μg/mL). The mixtures without as-prepared samples were taken as control.

2.6. Photothermal effect of different samples

The PBS solution of different samples (100 μg/mL) was irradiated under an 808 nm NIR laser (MLL-III from Changchun, China) at a density of 1.0 W/cm² for 15 min with the temperature recording every 30 s by a thermal probe (FLIR E6).

2.7. Bacteria-binding ability investigation

Gram-negative E. coli was taken as the target bacteria to investigate the bacteria-binding ability. The bacteria were cultured on the LB solid plate, and single colony was extracted and slowly dropped into the fluid nutrient medium. The fresh E. coli suspension can be obtained after incubation at 37 °C for 12 h in the water shaking bath. The E. coli was collected by centrifuging (5000 rpm, 3 min) and the E. coli suspension (~10⁷ cfu/mL) was formed by diluting with PBS (pH of 7.4). All the glassware in the experiments was kept at 121 °C for 20 min to guarantee sterility.

The different as-prepared samples (final concentration of 100 μg/mL) were mixed with 1 mL bacterial suspension containing ~10⁷ cfu/mL of E. coli. The mixture was incubated at room temperature in shaking bath for 30 min. The bacteria stuck onto the as-prepared samples were removed by magnetism. The bacteria mixed with MoS2 were collected by centrifuging at 1000 rpm for 1 min. The bacteria left in the suspension were withdrawn and diluted to proper concentrations, followed by being spread onto the sterilized LB agar plates. The viable colonies were enumerated and calculated.

2.8. Antibacterial experiments

The bacterial suspension (~10⁷ cfu/mL) was incubated with different concentrations (50 μmol/L, 100 μmol/L, 500 μmol/L, 1 mmol/L, 5 mmol/L, and 10 mmol/L) of H2O2. The antibacterial effect of different concentrations was examined by an oxford-cup method. The toxicity of different as-prepared samples was also investigated by an oxford-cup method.

The standard plate counting method was employed to investigate the antibacterial properties. The E. coli suspension (~10⁷ cfu/mL) was mixed with different samples: Fe3O4, MoS2, Fe3O4@MoS2, Fe3O4@MoS2-Ag, H2O2, Fe3O4+H2O2, MoS2+H2O2, Fe3O4@MoS2+H2O2 and Fe3O4@MoS2-Ag + H2O2 without and with 808 nm NIR laser irradiation for 15 min in the 24-well cell culture plates. The final concentrations of H2O2 and catalysts were 100 μmol/L and 100 μg/mL, respectively. After incubation for another 1 h at room temperature, 100 μL bacterial suspension was withdrawn and spread onto the LB solid plate for enumeration. The plates were cultured at 37 °C for 12 h, and the viable colonies can be observed. The E. coli with and without NIR irradiation was taken as the control. Each experiment was conducted at least three times.

To confirm the broad-spectrum antibacterial performance of this method, Staphylococcus aureus (S. aureus, ATCC6538), Bacillus subtilis (B. subtilis, ATCC6633), Methicillin-resistant Staphylococcus aureus (MRSA, ATCC43300) and Candida albicans (C. albicans, ATCC10231) were selected as the representatives of Gram-positive bacteria, drug-resistant bacteria and fungal bacteria for the antibacterial application. All experiments underwent following the aforementioned procedures. For the disinfection process, the optimal nanozyme at concentration of 100 μg/mL and H2O2 at concentration of 100 μmol/L were employed. Four groups of each kind of bacteria: I) bacteria control, II) bacteria + H2O2, III) bacteria + nanozyme and IV) bacteria + nanozyme + H2O2 were treated without and with 808 nm NIR laser irradiation for 15 min. The viable colonies on LB solid plates cultured at 37 °C after 12 h were enumerated via standard plate counting method. Each experiment was
conducted at least three times.

2.9. Morphology observation of live/dead bacteria

SEM images were obtained to observe the morphology changes of bacteria through different treatments. The bacteria with different samples were collected via centrifuging or magnetism. The mixture was treated by glutaraldehyde (2.5%) at 4 °C overnight. After fixation, the mixture was washed with distilled water. And then, gradual dehydration of bacteria was done by 10%, 30%, 50%, 70%, 90% and 100% ethanol treatment in sequence for separate 15 min. The final bacteria solution was dropped onto the silica substrate with gold coating for SEM observation. The fluorescence images of live/dead bacteria and magnetic recycle of the catalyst were described in supporting information.

3. Results and discussion

3.1. Synthesis and characterizations of Fe$_3$O$_4$@MoS$_2$-Ag

The nanozyme was constructed by engineering MoS$_2$ sheets on the surface of Fe$_3$O$_4$ nanoparticles with a two-step hydrothermal method. SEM image (Fig. 1a) showed the magnetic nanospheres of Fe$_3$O$_4$ with average diameter of ~335.6 nm in a narrow distribution. The TEM image (Fig. 1b) exhibited the typical pomegranate-like microstructure of Fe$_3$O$_4$ consisting of many small magnetic particles [36]. The inset image of Fig. 1b confirmed the polycrystal of Fe$_3$O$_4$ by electron diffraction in selected area (SAED). The Fe$_3$O$_4$@MoS$_2$-Ag composites were observed with MoS$_2$ covering Fe$_3$O$_4$ (diameter of ~428.9 nm) by SEM and TEM images (Fig. 1c and d). The Fe$_3$O$_4$ nanoparticle was employed as the support with irregular and curvy MoS$_2$ nanosheets vertically and densely growing on the surface to increase the exposed edges of MoS$_2$ layers and form the rough surface, followed by loading Ag nanoparticles on MoS$_2$ sheet surface (Fig. 1e). The morphology of MoS$_2$ was shown in Fig. S1a and b with sheet structure. The high resolution TEM image (Fig. 1f) clearly depicted the crystal lattice of 0.618 nm and 0.238 nm corresponding to the (002) plane of MoS$_2$ and the (111) plane of Ag nanoparticle, which revealed the formation of Ag nanoparticles (size of ~17 nm). Meanwhile, the discontinuous crystal lattice and atom loss in basal surface (Fig S1c and d) demonstrated the atom-vacancy defect in MoS$_2$ sheets, which is favorable for the enhancing adhesive ability [23].

The energy dispersive spectroscopic (EDS) mapping images (Fig. 1g, h, i and j) of Fig. 1c showed the even distribution of Fe, Mo, S and Ag elements in Fe$_3$O$_4$@MoS$_2$-Ag composites, which illustrated the coverage of MoS$_2$ on Fe$_3$O$_4$ and the uniform distribution of Ag inside the composites. The surface EDS elemental atomic ratio of Mo and S (Fig. S2) was determined to be 1:1.7, revealing the S-defect of MoS$_2$. Also, the zeta potential of as-prepared Fe$_3$O$_4$ at pH of ~7 was ~27.9 mV, while the zeta potential of MoS$_2$ at the same pH was ~20.2 mV. After the integration of MoS$_2$ on Fe$_3$O$_4$, the zeta potential at pH of ~7 was ~25.0 mV, which confirmed the wrapping of MoS$_2$. The negative charge facilitated the adsorption of Ag $^+$, which was beneficial for further in-situ photo-reduction. According to the ICP-MS results, the final loading amounts of Ag were 3.875, 8.500, 25.251 and 44.125 μg of Ag in 1 mg Fe$_3$O$_4$@MoS$_2$-0.5%Ag, Fe$_3$O$_4$@MoS$_2$-1%Ag, Fe$_3$O$_4$@MoS$_2$-3%Ag and Fe$_3$O$_4$@MoS$_2$-5%Ag, respectively. The mass ratio of Fe and Mo in prepared Fe$_3$O$_4$@MoS$_2$-Ag was determined to be ~1.71:1 by ICP-MS. After the deposition of Ag, the zeta potential of different composites at the same pH slightly increased from ~22.3 mV to ~21.4, ~21.1, ~20.9 mV with increasing loading amount of Ag (Fig. S3), respectively.

The XRD patterns of different samples were presented in Fig. 2a. The diffraction peaks at 18.2°, 30.1°, 35.4°, 37°, 43.1°, 53.4°, 56.9° and 62.5° were indexed to (111), (220), (311), (222), (400), (422), (511)
and (4 4 0) planes of face-centered Fe3O4 nanoparticles [37]. The typical peaks appearing at 14.8°, 32.5° and 57.5° responded to (002), (100) and (110) planes of MoS2 (JCPDS No. 75-1539) [38], which was in agreement with the TEM results. The XRD patterns of Fe3O4@MoS2-Ag exhibited the characteristic peak of Ag nanoparticles at 38° as well as the typical peaks of MoS2 and Fe3O4, which confirmed the construction of Fe3O4@MoS2-Ag composites. The weak peak of Ag was due to the relatively low loading amount of Ag nanoparticles. FT-IR spectra were used to testify the inorganic groups (Fig. S4). The spectrum of MoS2 confirmed the removal of thiourea. The peak around 586 cm⁻¹ belonged to Fe-O vibration. Meanwhile, the incorporation of Ag did not change the structures of the composites. Raman spectroscopy was also employed to explore the surface modification with a laser of 532 nm (Fig. 2b). The double peaks at ~378.8 and ~404.8 cm⁻¹ were attributed to the E2g and A1g vibrational modes of MoS2 [39], which showed slightly shift due to the coupling with Fe3O4 and Ag compared with those of pure MoS2. The chemical states of different elements in the composites were further investigated by XPS measurement. As shown in Fig. 2c, the broad survey spectrum of Fe3O4@MoS2-Ag composite contained the elements of Fe, O, Mo, S and Ag, demonstrating the components in the composite. Fig. 2d depicted the high-resolution spectra of Fe2p, where the characteristic binding energy peaks located at 724 and 711 eV assigned to Fe2p1/2 and Fe2p3/2 confirming the existence Fe3O4. In the Fe3O4@MoS2-Ag composite, the shifted peaks may be explained by the interaction of Fe with S by coupling with MoS2. Fig. 2e showed the specific information of Mo3d with two main peaks and two shoulder peaks. The two main distinct peaks can be fitted into two sets of 232.2 and 229.2 eV as well as 231.6 and 228.4 eV, which were attributed to 2H-MoS2 and 1T-MoS2, respectively. The peaks at 232 and 229 eV belonged to Mo3d3/2 and Mo3d5/2 of Mo (IV). The peak located at 235.3 eV was indexed to MoO2 due to the insufficient synthesis during hydrothermal process [40]. The peak centered at 225.6 eV was the result of S2s, accounting for the formation of 2H-MoS2 [41]. The characteristic peaks at 162.5 and 161.3 eV in Fig. 2f originated from S2p1/2 and S2p3/2 of S (II), respectively. For the Fe3O4@MoS2-Ag composite, the binding energy of S2p tinily shifted, which confirmed the interaction between S and Fe during the coupling of Fe3O4 and MoS2. The high-resolution spectrum of Ag in Fig. 2g exhibited two distinct peaks at 374.3 and 368.3 eV with a splitting energy of 6 eV corresponding to Ag3d3/2 and Ag3d5/2 of Ag (0) [42], which indicated the formation of metal Ag on the surface of MoS2. According to the specific surface XPS data of the Fe3O4@MoS2-Ag composite, the atom ratio of Mo and S was calculated to be 1:1.65, which verified the TEM and EDS results.

The BET analyses of different samples were carried out to investigate the specific surface area. The N2 adsorption-desorption isotherms of MoS2, Fe3O4, Fe3O4@MoS2 and Fe3O4@MoS2-1%Ag and corresponding pore width distributions were shown in Fig. S5. The curves of all samples exhibited obvious hysteresis at the relative high pressure (P/P0) between 0.6 and 1.0, which was in accordance with type IV isotherms. The BET surface area was calculated to be 7.746, 13.464, 16.607 and 17.446 m²/g for MoS2, Fe3O4, Fe3O4@MoS2 and Fe3O4@MoS2-1%Ag, respectively, showing the superiority of MoS2 sheets vertically growing on Fe3O4. Meanwhile, the Ag nanoparticles on MoS2 sheets slightly enhanced the specific surface area, which was favorable for the catalysis. Fig. S5b presented the wide pore width distribution of different samples centering between 2 and 25 nm, indicating the mesoporous nanostructure. The magnetic properties of different samples were investigated at 300 K (Fig. 2h). All samples exhibited good superparamagnetic properties with little hysteresis and coercivity, indicating the excellent magnetic response under magnetic fields. The magnetization saturation
values decreased from 76.9 emu/g for Fe$_3$O$_4$ to 39.8 emu/g for Fe$_3$O$_4$@MoS$_2$ and 33.3 emu/g for Fe$_3$O$_4$@MoS$_2$-Ag, which could be explained by the less mass ratio of Fe$_3$O$_4$ in unit composites [43]. The inset photos showed the rapid response (20 s) of Fe$_3$O$_4$@MoS$_2$-Ag to external magnetic field and the suspension quickly became even after removing the magnetism. The optical properties of different samples were investigated by UV–Vis-NIR spectrophotometer. Fig. S6a presented the UV–Vis-NIR diffuse reflectance spectra of different sample powders, which showed the good absorbance of MoS$_2$ from 300 to 1000 nm. An obvious absorbance region around 800 nm of Fe$_3$O$_4$ nanoparticles appeared mainly attributed to the tiny particles of a single nanoparticle. The surface modification of MoS$_2$ on Fe$_3$O$_4$ nanoparticles promoted its absorbance around 800 nm. The increased absorbance at ~420 nm is due to the surface plasmon resonance (SPR) effect of Ag nanoparticles on the surface of nanozymes, meanwhile the enhanced absorbance around 800 nm is possibly the result of the quick electron transfer by Ag nanoparticles. The UV–Vis-NIR absorbance spectra of different samples in aqueous solution displayed the similar trend as the UV–Vis-NIR diffuse reflectance spectra of corresponding powders (Fig. S6b), demonstrating excellent absorbance at ~800 nm of the as-prepared nanozymes in aqueous solution. The photothermal effect of different samples (100 µg/mL) at PBS (pH of 7.4) was conducted under an 808 nm NIR irradiation (1.0 W/cm$^2$). The temperatures were recorded every 30 s as shown in Fig. 2i. As the control, the PBS almost stayed a slight increase with $\Delta T$ of 2.7 °C in 15 min. The temperatures of all samples increased with the irradiation time, among which the temperature of MoS$_2$ increased to 43.3 °C and the temperature of Fe$_3$O$_4$ suspension increased to 45.4 °C after 15 min irradiation. For the coupling of these two components, the temperature reached a significantly higher temperature of 48.3 °C, while the incorporation of Ag improved the photothermal property to 50.7 °C, which displayed excellent photothermal effect of the composites. The photothermal effect of composites (100 µg/mL) with different Ag loading was investigated. Fig. S7a showed the temperature change of different samples. The temperature of Fe$_3$O$_4$@MoS$_2$-0.5%Ag irradiated after 15 min rose to 49.1 °C, while the final temperatures of Fe$_3$O$_4$@MoS$_2$-1%Ag, Fe$_3$O$_4$@MoS$_2$-3%Ag and Fe$_3$O$_4$@MoS$_2$-5%Ag were around 50.5 °C, exhibiting little difference. The higher temperatures were obtained with increasing concentrations of Fe$_3$O$_4$@MoS$_2$-Ag (Fig. S7b).

3.2. Investigation of peroxidase-like property

The peroxidase-mimicking properties of different as-prepared samples were investigated by fluorescent experiments and UV–Vis response
in different conditions. TPA was employed as the fluorescent probe to check the existence of OH, where higher intensity meant more OH. It can be found that TPA alone and H₂O₂ alone showed negligible fluorescent intensity at 435 nm after incubation for 6 h, while single TPA or H₂O₂ with catalyst did not show much difference in Fig. 3a. The intensity of TPA and H₂O₂ in the presence of catalyst exhibited greatly improvement, which suggested that the catalyst could convert H₂O₂ into -OH. The intensity gradually increased by chemical coupling Fe₃O₄ with MoS₂, and the addition of Ag nanoparticles also considerably increased the fluorescent intensity, which was due to the assisting adsorption of TPA by interaction between Ag nanoparticles and -COO- group in TPA. However, with more loading amount of Ag, the intensity of nanozymes increased. Fe₃O₄@MoS₂-1%Ag showed the strongest intensity. The peroxidase-like ability was subsequently verified with the catalytic oxidation of TMB monitored by UV-Vis spectrometer (Fig. 3b). The control experiment only contained H₂O₂ and TMB. After incubation for 5 min, a typical absorbance at 652 nm was observed with different as-prepared samples, whereas the control showed no absorbance, indicating no peroxidase reaction happened. The higher absorbance intensity referred to the strong peroxidase ability. The intensity of Fe₃O₄@MoS₂ was much higher than that of Fe₃O₄ alone and MoS₂ alone. The incorporation of Ag into Fe₃O₄@MoS₂ promoted the intensity by the enhanced -OH production property. Fe₃O₄@MoS₂-1%Ag showed the highest intensity. The peroxidase-mimicking ability can also be observed by the color change seen from the inset of Fig. 3b. The higher peroxidase-like property was, the darker blue the solution became, which confirmed the excellent peroxidase-like property of Fe₃O₄@MoS₂-1%Ag. Hence, the Fe₃O₄@MoS₂-1%Ag was chosen as the optimal sample for the further kinetic study and antibacterial applications.

The kinetic study of the catalytic process in our work was analyzed according to Michaelis-Menten equation. The Michaelis Menten constant (Kₘ) was calculated through the Lineweaver Burk plot:

\[
\frac{1}{v} = \frac{K_m}{V_{max}} \times \frac{1}{[S]} + \frac{1}{V_{max}}
\]

Vₜ was obtained through the absorption intensity at 652 nm and the molar absorption coefficient of oxidation product of TMB (39000/ (cm·mol/L)) [44]. Based on the above parameters, the Michaelis-Menten curves of Fe₃O₄@MoS₂-1%Ag were measured by separately manipulating the concentrations of TMB (Fig. 3c and d) and H₂O₂ (Fig. 3e and f). As a contrast, the Michaelis-Menten curves of Fe₃O₄@MoS₂ were shown in Fig. 58. Kₘ and Vₚₘₐₓ of different samples were obtained through the formulation (Table S1). Normally, the lower Kₘ represents the stronger attraction between the catalyst and the substrate, while the higher Vₚₘₐₓ refers to the better catalytic ability. The whole catalytic process should be assessed by combining Kₘ and Vₚₘₐₓ.

Compared to the data of HRP in previous reports [45], both Fe₃O₄@MoS₂ and Fe₃O₄@MoS₂-1%Ag showed smaller values of Kₘ, indicating better affinity to TMB and H₂O₂ to promote catalytic performance, which makes it possible to act as peroxidase. Moreover, the value of Vₚₘₐₓ of Fe₃O₄@MoS₂-1%Ag was a little higher than that of Fe₃O₄@MoS₂, which may be the result of peroxidase-like and electron transfer accelerating property of Ag [46].

Similar to the natural enzyme, the catalytic response of Fe₃O₄@MoS₂-1%Ag to pH and temperature was also considered. As shown in Fig. 59, Fe₃O₄@MoS₂-1%Ag composites exhibited best catalytic activity at pH of 4. With the increasing pH, the relative activity of Fe₃O₄@MoS₂-1%Ag decreased, but it still showed catalytic capability at pH of 7.4, which was favorable for the in vivo disinfection treatment. Unlike natural enzyme, the artificial nanozyme showed increasing catalytic activity with the higher temperature in the range from 25 to 55 °C. Besides, four groups of (i) TMB only (1 mmol/L), (ii) TMB and H₂O₂ (1 mmol/L), (iii) TMB and Fe₃O₄@MoS₂-1%Ag (50 μg/mL), (iv) TMB, Fe₃O₄@MoS₂-1%Ag and H₂O₂ were irradiated by 808 nm NIR laser to examine the influence of hyperthermia on POD-like activity. Fig. S10a clearly showed the UV–Vis absorbance spectra with strong absorbance at 652 nm of TMB, Fe₃O₄@MoS₂-1%Ag and H₂O₂ mixture without NIR irradiation, which indicated the increased catalytic reaction with time at room temperature. Fig. S10b exhibited the UV–Vis absorbance spectra of the same mixture composition with that in Fig. S10a under 808 nm laser irradiation. The intensity at 652 nm of the mixtures without and with irradiation was recorded in Fig. S10c. The catalytic reaction in mixture under irradiation showed growingly difference with that of mixture without irradiation for the same reaction time, which was due to the increased temperature with time caused by Fe₃O₄@MoS₂-1%Ag under 808 nm irradiation. Hence, POD-like activity of Fe₃O₄@MoS₂-1%Ag can be evidently promoted by hyperthermia from Fe₃O₄@MoS₂-1%Ag under 808 nm irradiation.

3.3. The adhesive properties against E. coli

The adhesive properties of different samples were explored against the fresh E. coli suspension with concentration of 10⁷ cfu/mL. The E. coli suspension was incubated with different samples: (I) control; (II) Fe₃O₄; (III) MoS₂; (IV) Fe₃O₄@MoS₂; (V) Fe₃O₄@MoS₂-1%Ag for 30 min. And then MoS₂ with E. coli was collected by centrifuging at 1500 rpm, while all other samples with attached E. coli were removed by external magnetic field. The E. coli suspensions left were spread on the agar plate and cultured for 24 h. The viable colonies were shown in Fig. S11a with decreasing numbers from group (I) to group (IV). Specifically, Fig. 4c showed that Fe₃O₄ only took away 4.2% E. coli, while MoS₂ adhered 5.7% E. coli. Regarding Fe₃O₄@MoS₂ and Fe₃O₄@MoS₂-1%Ag, the removal rate against E. coli of Fe₃O₄@MoS₂-1%Ag (~22.5%) was almost the same as that of Fe₃O₄@MoS₂ (~21.9%). The promising adhesive ability was promoted by surface engineering of sharp MoS₂ sheet, which was beneficial for the disinfection treatment. The morphology of removed as-prepared samples was observed by SEM images in Fig. S11b. It can be clearly seen that the viable E. coli was integral rhodactiform with no deformation and surface damage. Several E. coli without deformation was observed inside the Fe₃O₄ nanoparticles, which were extracted by the crowded particles. There were a few bacteria inside the MoS₂ sheets with the nanosheets around bacteria with slight deformation, showing the little adhesive ability. Unsurprisingly, more E. coli was found attaching to Fe₃O₄@MoS₂ and Fe₃O₄@MoS₂-1%Ag, which confirmed the enhanced interaction between bacteria and the catalyst. The deforma
tion with little destruction on the bacterial membrane of the E. coli attached to the surface of Fe₃O₄@MoS₂ and Fe₃O₄@MoS₂-1%Ag confirmed the notable adhesive ability of the catalysts due to the rough surface formed by sharp MoS₂ sheets engineered on Fe₃O₄ nanoparticles, which would be an essential part for the highly efficient attacking during disinfection process. Besides, the interaction between different samples and bacteria was further investigated. The cell wall of E. coli was mainly composed of peptidoglycan with amino acid residues with negative charge (Fig. S12), which acted as the functional sites to tightly combine with S-vacancy of S-defect MoS₂ to form chemical bonds [47,48]. It is also confirmed by phase transfer of samples from water to oil phase with oleylamine (–NH₂) and oleic acid (–COOH) as the hydrophobic ligands. Fig. S13 showed great affinity of Fe₃O₄@MoS₂ to –NH₂ and Fe₃O₄@MoS₂-1%Ag to both –NH₂ and –COOH. Hence, the pilus on bacteria and the sharp MoS₂ sheets first pierced the energy barrier between the two negatively charged objects. The interaction between Fe₃O₄@MoS₂-1%Ag and –NH₂ and –COOH facilitated the further affinity. The chemical bonds provided the potent adhesion of Fe₃O₄@MoS₂-1%Ag to bacteria.

3.4. In vitro antibacterial experiments

Considering its excellent peroxidase-like property and promising adhesive ability, the antibacterial performance was further evaluated against E. coli by a standard plate counting method. Because H₂O₂ at high concentration could result in damage to organism, the toxicity of H₂O₂ in different concentrations was assessed by oxford-cup method prior to antibacterial experiments. Fig. S14a demonstrated that H₂O₂ at
a low concentration of 100 \mu mol/L barely prohibited the growth of E. coli, while H₂O₂ at concentration of 500 \mu mol/L and 1 mmol/L could inhibit the growth inside the oxford cup. H₂O₂ at concentration of 5 and 10 mmol/L displayed extended inhibition zones. Thus, H₂O₂ at a moderate concentration of 100 \mu mol/L was the optimal concentration for future use. The disinfection performance was tested in different groups: (I) PBS control, (II) H₂O₂, (III) Fe₃O₄, (IV) MoS₂, (V) Fe₃O₄@MoS₂, (VI) FeO₄@MoS₂-1%Ag, (VII) Fe₃O₄ + H₂O₂, (VIII) MoS₂ + H₂O₂, (IX) Fe₃O₄@MoS₂ + H₂O₂, (X) FeO₄@MoS₂-1%Ag + H₂O₂ without and with 808 nm NIR irradiation at a density of 1.0 W/cm². As presented in Fig. 4a and b, negligible inhibition against E. coli could be observed when cultured with Fe₃O₄, MoS₂, FeO₄@MoS₂ and FeO₄@MoS₂-1%Ag (100 \mu g/mL) without NIR irradiation, implying their insignificant damage on E. coli, which could be confirmed by the oxford-cup method with almost no inhibition zone around the samples (Fig. S12b). The SEM images showed no obvious destruction on the surface structure of the bacteria, indicating that the FeO₄@MoS₂-1%Ag could not cause fatal damage on bacteria. By combining the catalysts with H₂O₂ distinctly reduced viable colonies were shown with decreasing survival percentage of 92.1%, 90.3%, 80.0% and 69.4% for groups of Fe₃O₄, MoS₂, FeO₄@MoS₂ and FeO₄@MoS₂-1%Ag, respectively, illustrating the significant role of produced •OH. SEM images confirmed the partial deformation and membrane damage of the E. coli. Subsequently, photothermal effect was used to assist the antibacterial treatment. The result of PBS control group as well as the H₂O₂ alone group demonstrated little influence of NIR irradiation against viable E. coli. The visual colony numbers of different samples under irradiation without H₂O₂ evidently decreased, which illustrated that the hyperthermia could effectively cause the bacteria destruction (Fig. 4b). Obviously, the survival percentage of FeO₄@MoS₂-1%Ag (46.6%) was much lower than that of FeO₄@MoS₂ (60.3%), indicating that the higher temperature showed better disinfection performance. After combining with the moderate concentration of H₂O₂ under NIR irradiation, the survival percentages of different groups continued reducing, implying the enhanced antibacterial ability due to the increasing property to convert H₂O₂ into highly toxic •OH and the heat. FeO₄@MoS₂-1%Ag showed prominent antibacterial performance that nearly disinfected all bacteria, which was better than FeO₄@MoS₂ with survival percentage of 13.5%. The survival rates of all samples at different conditions were exhibited in Fig. 4d. SEM images verified the morphology of bacteria together with catalysts, where the bacteria were apparently adhesive to Fe₃O₄, MoS₂ and FeO₄@MoS₂-1%Ag with distorted and destroyed membrane. It can be deduced that the adhesive ability of FeO₄@MoS₂-1%Ag paved the way for interaction between bacteria and catalyst, and at the same time the collaborative work of •OH and hyperthermia dominated the accurate disinfection process.

A concentration-dependent disinfection study was explored with ten groups: E. coli, E. coli + H₂O₂, E. coli + FeO₄@MoS₂-0.5%Ag, E. coli + H₂O₂ + FeO₄@MoS₂-0.5%Ag, E. coli + FeO₄@MoS₂-1%Ag, E. coli + H₂O₂ + FeO₄@MoS₂-1%Ag, E. coli + FeO₄@MoS₂-3%Ag, E. coli + H₂O₂ + FeO₄@MoS₂-3%Ag, E. coli + FeO₄@MoS₂-5%Ag, E. coli + H₂O₂ + FeO₄@MoS₂-5%Ag without and with 808 nm NIR irradiation for 15 min. The viable colonies of E. coli in each group were enumerated and disinfection results were calculated by standard agar plate method. The viable colonies and survival rates of different samples without NIR irradiation (Figs. S15 and S16) manifested that all composites alone
cannot affect the growth of bacteria. However, the numbers of *E. coli* incubated with different samples and irradiated by NIR exhibited clear decrease, indicating the roles of hyperthermia against bacteria. The *E. coli* incubated with different samples and H$_2$O$_2$ without NIR irradiation also deceased in agreement with the POD-like properties, showing the •OH attack on bacteria. As with the synergistic effect, ~6% of *E. coli* with Fe$_3$O$_4$@MoS$_2$-0.5%Ag and H$_2$O$_2$ under NIR irradiation were still alive, whereas the *E. coli* with other samples were all dead, implying the prominent disinfection performance of all samples. Moreover, ICP-MS was employed to detect the released Ag$^+$ during the 15 min treatment in four groups of only nanozyme (100 μg/mL), nanozyme (100 μg/mL) and 808 nm NIR irradiation, nanozyme (100 μg/mL) and H$_2$O$_2$ (100 μmol/L), and nanozyme (100 μg/mL), H$_2$O$_2$ (100 μmol/L) and 808 nm NIR irradiation. Fig. S17a displayed the increased Ag$^+$ leakage with the increased Ag load in samples. The hyperthermia caused by NIR irradiation and oxidizing of H$_2$O$_2$ could accelerate the Ag$^+$ leakage. The released Ag$^+$ could play an auxiliary role in disinfection process and enhanced the antibacterial performance. The highest amount of released Ag$^+$ in Fe$_3$O$_4$@MoS$_2$-1%Ag suspension was 62.6 μg/L. Fig. S17b showed the releasing trend of Ag$^+$ in Fe$_3$O$_4$@MoS$_2$-1%Ag incubated with H$_2$O$_2$ under NIR irradiation, indicating the gradual release of Ag$^+$ with time.

The rupture of *E. coli* incubated with different catalysts under 808 nm NIR irradiation was examined by blue fluorescence (DAPI) staining all bacteria and PI staining membrane-damaged *E. coli*. As shown in Fig. 5a, the fluorescence images demonstrated that the NIR irradiation of PBS and H$_2$O$_2$ cannot destroy the membrane integrity and cause the red fluorescence stains. When the *E. coli* suspension with different catalysts was irradiated by 808 nm for 15 min, the fluorescence images showed increasing red fluorescence stains with the higher temperature by photothermal effect, which illustrated that the local hyperthermia can cause the membrane disorganization of *E. coli*. The number of red fluorescence stains rose in the presence of H$_2$O$_2$, implying the attack of •OH towards the bacterial membrane. Compared with Fe$_3$O$_4$@MoS$_2$, Fe$_3$O$_4$@MoS$_2$-1%Ag showed the highest numbers of dead bacteria, which was in agreement with the results of viable colonies on agar plates. The micro structure of single *E. coli* was further observed by SEM images. It can be seen that the fresh live *E. coli* was smooth and rod-like with intact membrane, while the bacteria treated by H$_2$O$_2$ showed no obvious difference on the structure. All the dead bacteria exhibited the clear deformation and disruption of membrane, finally resulting in the leakage of cytoplasm. Based on above description, the possible synergetic antibacterial mechanism was that the adhesion of Fe$_3$O$_4$@MoS$_2$-1%Ag to bacteria facilitated the precise and rapid attacking of •OH caused by peroxidase-like property and Ag$^+$ leaking from the catalyst surface assisted by the local hyperthermia under 808 nm NIR irradiation, thus leading to the deformation and disruption of bacterial membrane with leakage of cytoplasm. Fe$_3$O$_4$@MoS$_2$-1%Ag was recycled by external magnetic field and reuse to disinfect *E. coli*, which showed excellent inactivation rate (~95%) and stability after 5 times reuse (Fig. S18).

The broad-spectrum antibacterial performance of Fe$_3$O$_4$@MoS$_2$-1%Ag was confirmed by their disinfection effect on *S. aureus*, *B. subtilis*, MRSA and *C. albicans*. Fig. S19a and b showed disinfection results of *S. aureus*. The viable colonies on standard agar plates exhibited no difference in *S. aureus*, *S. aureus* + NIR, *S. aureus* + H$_2$O$_2$, *S. aureus* + H$_2$O$_2$.
was possibly due to the component difference of membranes. The viable perthermia than and universal towards ~57% of S. aureus was disinfected by the treatment of Fe$_2$O$_3$@MoS$_2$-1%Ag, H$_2$O$_2$ and NIR due to the synergistic effect of OH, hyperthermia and Ag$^+$. Fig. S19c and d displayed the morphology change of S. aureus of fresh cells and treated cells. The excellent disinfection performance was universal towards B. subtilis (Fig. S20a and b), MRSA (Fig. S21a and b) and C. albicans (Fig. S22a and b). B. subtilis was more sensitive to hyperthermia than OH, while MRSA showed the contrary result, which was possibly due to the component difference of membranes. The viable colonies of both bacteria dramatically decreased under treatment of OH, hyperthermia and Ag$^+$. For C. albicans, OH or hyperthermia alone killed small portion of C. albicans, while the synergy of them damaged 80% of C. albicans. The SEM images of all morphology comparisons between fresh cells and dead cells distinctly elucidated the damage on cell membranes of dead cells (Fig. S20c and d, Fig. S21c and d, Fig. S22c and d). The abovementioned results confirmed the broad-spectrum antibacterial property of Fe$_2$O$_3$@MoS$_2$-1%Ag against Gram-negative bacteria, Gram-positive bacteria, drug-resistant bacteria and fungal bacteria.

4. Conclusion

In summary, a facile artificial nanzyme of Fe$_2$O$_3$@MoS$_2$-1%Ag was constructed by a two-step hydrothermal method with in-situ growth of Ag nanoparticles. The composite showed attractive rough surface by engineering sharp MoS$_2$ sheet around Fe$_2$O$_3$ surface, which exhibited potent adhesive ability towards bacteria. The peroxidase-mimicking properties were further explored by TMB and TPA, which confirmed the effective converting a low concentration of H$_2$O$_2$ into toxic OH. When exposed to 808 nm NIR irradiation, the local hyperthermia and enhanced peroxidase-mimicking property can prominently improve the disinfection activity. The antibacterial experiments against E. coli revealed that Fe$_2$O$_3$@MoS$_2$-1%Ag can efficiently inactivate bacteria by capturing E. coli and releasing toxic OH and Ag$^+$ assisted by local hyperthermia to attack the membranes. The magnetic property made it feasible to reuse it. The broad-spectrum antibacterial performance against Gram-negative bacteria, Gram-positive bacteria, drug-resistant bacteria and fungal bacteria was demonstrated. The fabrication of this nanzyme with promising adhesive ability would effectively shorten the diffusive distance of OH, which provided a potential option for rapid and effective antibacterial treatment.

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.

Acknowledgements

This work was supported by the National Key R & D Program of China (2017YFA0207203), the National Natural Science Foundation of China (Grant No. 21773050), the Harbin Distinguished Young Scholars Fund (No. 2017RAYJX024), and the State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No. 2020DX03).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2020.127240.
W. Yin, J. Yu, L. Yan, L.R. Zheng, Z. Gu, Y. Zhao, Functionalized nano-MoS$_2$ with peroxidase catalytic and near-infrared photothermal activities for safe and synergistic wound antibacterial applications, ACS Nano 10 (2016) 11000–11011.

W.-N. Wang, C.-Y. Zhang, M.-F. Zhang, P. Pei, W. Zhou, Z.-B. Zha, M. Shao, H.-S. Qian, Precisely photothermal controlled releasing of antibacterial agent from Bi$_2$S$_3$ hollow microspheres triggered by NIR light for water sterilization, Chem. Eng. J. 381 (2020), 122630.

K. Zhao, W. Gu, S. Zheng, C. Zhang, Y. Xian, SDS–MoS$_2$ nanoparticles as highly-efficient peroxidase mimetics for colorimetric detection of H$_2$O$_2$ and glucose, Talanta 141 (2015) 47–52.

N. Guo, H. Li, X. Xu, H. Yu, Hierarchical Fe$_3$O$_4$@MoS$_2$/Ag$_3$PO$_4$ magnetic nanocomposites: enhanced and stable photocatalytic performance for water purification under visible light irradiation, Appl. Surf. Sci. 389 (2016) 227–239.

F. Wei, J. Li, C. Dong, Y. Bi, X. Han, Plasmonic Ag decorated graphitic carbon nitride sheets with enhanced visible-light response for photocatalytic water disinfection and organic pollutant removal, Chemosphere 242 (2020), 125201.

X. Xu, C. Deng, M. Gao, W. Yu, P. Yang, X. Zhang, Synthesis of magnetic microspheres with immobilized metal ions for enrichment and direct determination of phosphopeptides by matrix-assisted laser desorption ionization mass spectrometry, Adv. Mater. 18 (2006) 3299–3293.

X. Liang, X. Wang, J. Zhang, Y. Chen, D. Wang, Y. Li, Synthesis of nearly monodisperse iron oxide and oxyhydroxide nanocrystals, Adv. Funct. Mater. 16 (2006) 1805–1813.

H. Ramakrishna Matte, A. Gomathi, A.K. Manna, D.J. Late, R. Datta, S.K. Pati, C. Rao, MoS$_2$ and WS$_2$ analogues of graphene, Angew. Chem. Int. Ed. 49 (2010) 4059–4062.

Q. Gao, X. Zhang, W. Yin, D. Ma, C. Xie, L. Zheng, X. Dong, L. Mei, J. Yu, C. Wang, Functionalized MoS$_2$ nanovehicle with near-infrared laser-mediated nitric oxide release and photothermal activities for advanced bacteria-infected wound therapy, Small 14 (2018) 1802290.

T. Lin, J. Wang, L. Guo, F. Fu, Fe$_3$O$_4$@MoS$_2$ core–shell composites: preparation, characterization, and catalytic application, J. Phys. Chem. C 119 (2015) 13658–13664.

M. Zhu, X. Liu, L. Tan, Z. Cui, Y. Liang, Z. Li, K.W.K. Yeung, S. Wu, Photo-responsive chitosan/Ag/MoS$_2$ for rapid bacteria-killing, J. Hazard. Mater. 383 (2020), 121122.

T. Chen, X. Wu, J. Wang, G. Yang, WSe$_2$ few layers with enzyme mimetic activity for high-sensitive and high-selective visual detection of glucose, Nanoscale 9 (2017) 11806–11813.

P. Zhang, Z. Wang, L. Liu, L.H. Klausen, Y. Wang, J. Mi, M. Dong, Modulation the electronic property of 2D monolayer MoS$_2$ by amino acid, Appl. Mater. Today 14 (2019) 151–158.

E. Satheshkumar, A. Bandyopadhyay, M. Sreedhar, S.K. Pati, C. Rao, M. Yoshimura, One-step simultaneous exfoliation and covalent functionalization of MoS$_2$ by amino acid induced solution processes, ChemNanoMat 3 (2017) 172–177.