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Magnetic rod-based metal-organic frameworks metal composites for colorimetric detection of hydrogen peroxide (H_2O_2) and pollutant elimination.

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Abstract: Hydrogen peroxide (H_2O_2) is an important oxidizing agent that plays a crucial role in the food and beverage industry, the pharmaceutical industry, environmental fields amongst others. However, as a by-product of metabolic oxidation processes, it poses an immediate danger to life and health when concentrations are beyond the minimum threshold limit of 75 ppm. The detection of H_2O_2 is therefore of prime importance. Herein, a simple colorimetric assay for the detection of H_2O_2 based on the peroxidase-like mimetic activity of Fe_3O_4@MIL-100(Fe)-Au nanozyme was established. The triad-component nanozyme was synthesized by growing a five-layer MIL-100(Fe) metal-organic framework(MOF) around the magnetic Fe_3O_4 nanorod core and finally deposited gold on the core-shell structure. The oxidation of colorless 3,3,5,5 - tetramethylbenzidine to blue by H_2O_2 is very slow. The addition of the nanozyme increases the oxidation process. The magnetic property of the nanozyme was further harnessed to enhance the oxidation process on a magnetic field. The versatility of the as-prepared Fe_3O_4@MIL-100(Fe)-Au was demonstrated by applying it for the catalytic degradation 4-nitrophenol. The magnetic property was subsequently harnessed to enhance the catalytic degradation of the organic pollutant and also to conveniently effect separation of the catalyst after application. Besides the catalysis, the magnetic property of the composite was utilized to enhance the adsorption of bacteria pathogen. We believe such magnetic MOF-based composites have potential applications in many fields including microreactor systems.

Keywords: nanozyme; metal-organic framework; peroxidase; catalysis; adsorption

1. Introduction

Nanomaterials, materials of microscopic dimensions have gained significant attention in recent years due to their outstanding properties such as optical properties, surface area, relative ease of synthesis, versatility in applications as a result of their size among others[1]. To enhance their properties and potential applications, nanomaterials are incorporated into other functional materials to obtain composite materials that were even inconceivable in the latter parts of the twentieth century. These materials are at the forefront of modern research and the synergistic effects on the properties of such materials including metal-organic frameworks, their composites and derivatives have resulted in their applications in several fields with amazing results[2]. They have successfully been

applied in biomedicine for cancer imaging and therapy, as antimicrobials, for energy storage, gas separation and storage, catalysis, environmental monitoring and remediation among others[3–6]. Recently, nano-based materials such as MOFs have also been deployed as nanozymes, the umbrella term for an emerging paradigm that encompasses a large number of artificial nanomaterials and their composites with intrinsic enzyme-like activities[7]. They have been used for the detection of environmental pollutants, biosensing, etc.[8].

Hydrogen peroxide is an important chemical compound whose beneficial properties are still being explored and discoveries being made two centuries after its first successful synthesis by Thenard. Environmental concerns over deleterious chlorine-based bleaches used in the paper and allied industry resulted in the replacement of chlorine with H_2O_2 as a bleaching agent in paper production. As a consequence, the global demand for H_2O_2 has increased tremendously in the last decade[9]. Presently, H_2O_2 has numerous applications from biomedicine to environmental remediation. It is applied as a mild antiseptic on the skin to prevent infections from minor cuts, and as a mouthwash in dentistry to reduce plaque and improve recovery after oral surgery[10]. During the recent outbreak of SARS CoV-2 (COVID -19), officials at Duke University and Health System successfully decontaminated N95 respirators with vaporized H_2O_2[11–13]. Industrially, H_2O_2 is used as a green oxidant in processes such as in the synthesis of propene epoxide, etc in the fine chemical industry [9,14,15]. It also plays a major role in food processing and environmental remediation[16]. Despite these overwhelming beneficial applications of H_2O_2, its presence in the human body beyond a critical threshold limit (75 ppm) is detrimental to health and can result in cell damage, inflammatory disease, cancer, etc[16–18]. The detection of H_2O_2 is therefore of great importance due to its cytotoxicity. In this work, a magnetic MOF metal composite, Fe_3O_4@MIL-100(Fe)-Au was synthesized and applied as a nanozyme for the colorimetric detection of H_2O_2. Furthermore, the magnetic property of the nanozyme was utilized to enhance the kinetics (rate) of colorimetric detection on a magnetic field. In addition, the versatility of the synthesized composite was demonstrated by applying it for the degradation of 4-nitrophenol. Not only was the magnetic property of the composite used to enhanced the catalysis of 4-nitrophenol but also to effect separation. In addition, the property synergies of the composite were utilized for the adsorption of bacteria from solution.

2. Materials and Methods

The synthesis of Fe_3O_4@MIL-100(Fe)-Au followed three steps namely; the production of rod-shaped magnetite from rod-shaped β-FeOOH, the growth of MOF on the magnetite and the final deposition of Au on the coreshell structure. Rod-shaped β-FeOOH prepared as previously reported with slight modifications[19,20]. Briefly, 1.08 g of $FeCl_3.6H_2O$ and 1.0 g of CTAB were dissolved in 40 mL of deionized water. The mixture was heated at 87 ºC for 12 hours under gentle stirring. After hydrolysis, the mixture was separated and the precipitate was washed with deionized water severally. The obtained precipitate (β-FeOOH) was functionalized with polyacrylic acid (PAA) and reduced in tetraethylene glycol solution at 240 ºC in nitrogen (N_2) environment for 8 hours. The obtained magnetic nanorods were washed severally to remove the residual chemical. Layer by layer approach was then used to build 5-layers of MOF shell around the magnetic core as previously established [21]. 20 mg equivalent of the functionalized magnetic Fe_3O_4 nanorod was immersed in $FeCl_3.6H_2O$ ethanol solution (10 mM, 4 mL) for 20 minutes at 70 ºC and trimesic acid ethanol solution (10 mM, 4 mL) for 40 minutes separately at 70 ºC. Between each step, the nanorods were washed with

ethanol and separated (process repeated for 5-cycles). Finally, reduced $HAuCl_4$ was deposited on the magnetic core-shell structure[22] to obtain the final composite, Fe_3O_4@MIL-100(Fe)-Au. A summary of the synthesis procedure is illustrated in Figure 1 below.

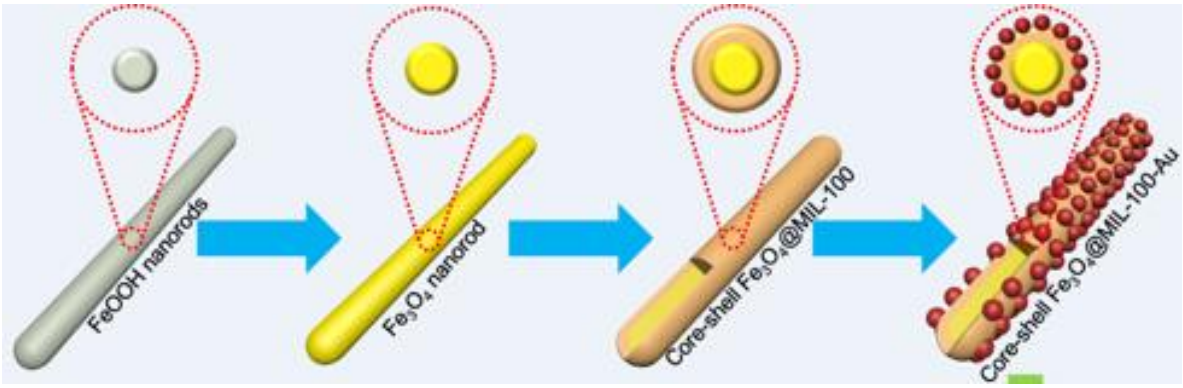

Figure 1. Schematic illustration of the synthesis of Fe_3O_4@MIL-100(Fe)-Au

The application studies was carried out by utilizing the synthesized composite for colorimetric detection of H_2O_2, degradation of 4-nitrophenol and the capture of bacteria. The peroxidase mimetic activity and the effect of the magnetic property of Fe_3O_4@MIL-100(Fe)-Au were elucidated using reported protocol with slight modification[16]. Fe_3O_4@MIL-100(Fe)-Au (4 mg/mL, 100 μL) was added to sodium acetate-acetic acid buffer solution (pH =4, 2400 μL) followed by the addition of TMB solution (1.55mM in ethanol, 480 μL) and H_2O_2(30%, 100 μL). The reaction mixture was incubated for 5 minutes and subsequently followed by UV/vis analysis taking note of the absorbance at 652 nm. The colorimetric detection was carried out on a magnetic field and without magnetic field.

For the degradation of 4-nitrophenol, 4 mL of freshly prepared $NaBH_4$ solution (0.2 M) was mixed with 6 mL of 4-NP solution (0.18 mM) and 4 mg of Fe_3O_4@MIL-100(Fe)-Au was added to the mixture. The progress of the reaction was monitored by taking the UV-vis spectra at successive intervals. The same reduction experiment was repeated on a magnetic field for comparison purposes. At the end of each run, the composite was separated with a magnet, rinsed with deionized water, and reapplied for the next run.

For the bacteria adsorption experiment, the composite was conjugated with salmonella antibody and applied for the capture of salmonella pathogen both on a magnetic field and a stationary system (non-magnetic field). The samples were stimulated at 488 nm and the corresponding fluorescence intensities were measured and capture rates determined.

3. Results and discussion

3.1. Characterization

3.1.1. Transmission electron microscopy (TEM) and elemental analysis

The TEM image in Figure 2 confirms the successful synthesis of rod-shaped magnetite structures, the successful growth of MIL-100 (Fe) shells, and the deposition of Au to form Fe_3O_4@MIL-100(Fe)-Au. The accompanying elemental analysis also gives credence to the presence of the expected major elements in the composite (Au, C, Fe, and O)

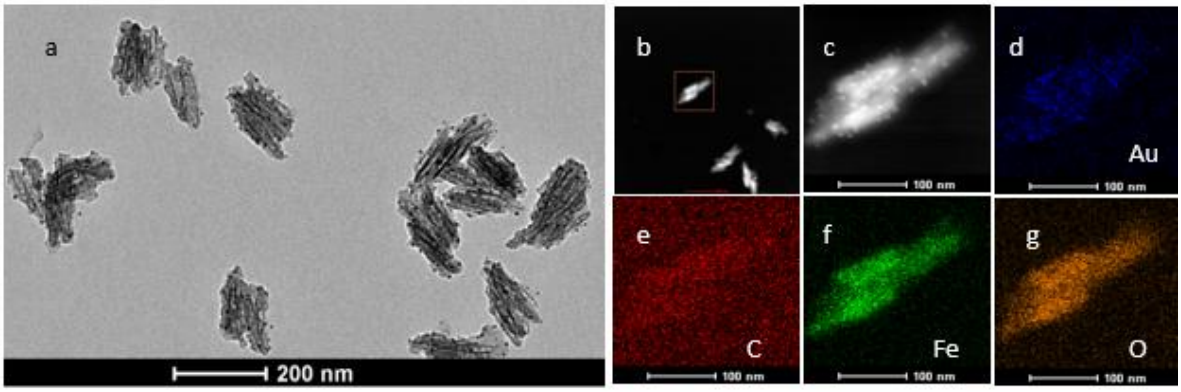

Figure 2. a) TEM image of Fe_3O_4@MIL-100(Fe)-Au; b, c) STEM HAADF image of composite; Corresponding elemental analysis results d) Au e) C f) Fe and g) O

3.1.2. X-ray diffraction (XRD) analysis

The X-ray diffraction analysis of the synthesized materials as exhibited in Figure 3a below shows the presence of Au with the characteristic peaks at 2θ =38.2, 44.4, 64.6, and 77.5º. The characteristic peaks of magnetite and MIL-100(Fe) as observed conforms with similar observations for Fe_3O_4@MIL-100(Fe) in literature[23].

3.1.3. Fourier transform infrared(FTIR) spectroscopy

The acquired FTIR as shown in Figure 3b below also confirms the formation of the synthesized composite. The characteristic stretching-vibration bands between 3200 and 3600 cm^{-1} which peaks at 3423 cm^{-1} are indicative of OH functional groups in the preparation of Fe_3O_4. The bands at 1550 and 1437 cm^{-1} are attributable to the C=C stretching vibrations of carboxylic acid thereby confirming the growth of MIL-100(Fe).

3.1.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the synthesized material and to demonstrate the successful formation of Fe_3O_4@MIL-100(Fe)-Au. As illustrated in Figure 3c, a comparison of Fe_3O_4@MIL-100(Fe)-Au and Fe_3O_4@MIL-100(Fe) reveals better stability of the composite. This can be attributed to the synergistic effect of the individual components. Besides, the significant weight loss observed in Fe_3O_4@MIL-100(Fe) is an affirmation of the successful growth of MIL-100(Fe) on the magnetite core. The successful deposition of Au results in less weight loss.

3.1.5. Vibrating-sample magnetometer (VSM) analysis

The magnetic property is an important feature of the prepared composite. As shown in Figure 3d, the magnetization saturation value for the composite was 40 emu/g whiles that of Fe_3O_4 nanorod was 62 emu/g. The observed difference in magnetization saturation value is due to the effect of the non-magnetic components (Au and MIL-100(Fe)) on the synthesized Fe_3O_4@MIL-100(Fe)-Au.

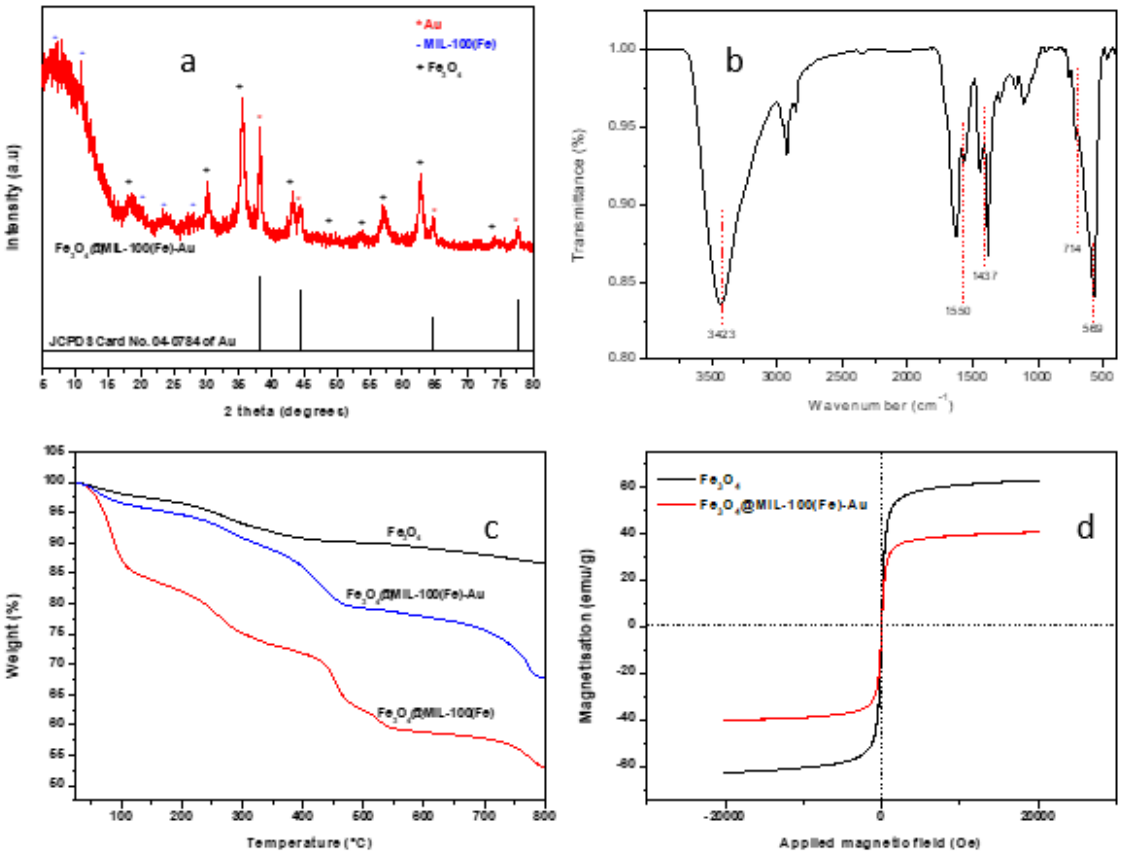

Figure 3. a) XRD pattern for Fe_3O_4@MIL-100(Fe)-Au; b) FTIR spectra for Fe_3O_4@MIL-100(Fe)-Au; c) Thermogram of Fe_3O_4, Fe_3O_4@MIL-100(Fe), and Fe_3O_4@MIL-100(Fe)-Au; d) VSM plot for Fe_3O_4 and Fe_3O_4@MIL-100(Fe)-Au

3.2. Application

3.1.1. Hydrogen peroxide (H_2O_2) detection

The enzyme mimetic activity of the composite was utilized for the detection of H_2O_2. The oxidation of the colorless TMB to blue by H_2O_2 after incubation for 5 minutes is very slow (no obvious color change is observed) as shown in the picture and UV-vis spectra in Figure 4. However, upon the addition of the nanozyme, blue color is observed after the same incubation period (Inset: middle picture). A deep blue color was observed when the nanozyme was applied to the reaction mixture on a magnetic field for the same duration of incubation(Inset: left picture). The observed change in coloration from blue to deep blue is due to the improved kinetics as a result of the stirring effect of the nanozyme on the magnetic field. As confirmed by the associated UV-vis spectra, the magnetic property of the nanozyme has been successfully utilized to enhance the colorimetric detection of H_2O_2 (Figure 4). The observed results show that similar composites have potential applications as nanosensors.

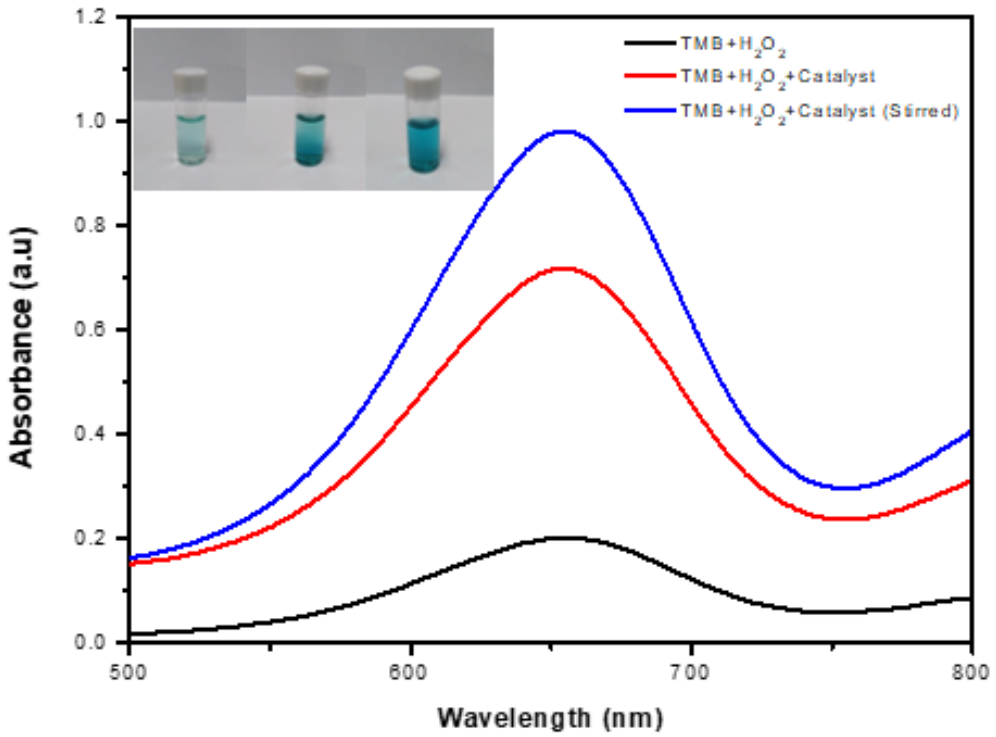

Figure 4. UV-vis spectra for TMB oxidation with H_2O_2 without nanozyme (black), with nanozyme(red), and with nanozyme on a magnetic field (blue) (Inset picture: TMB+H_2O_2 (left), TMB +H_2O_2+Nanozyme (middle), and TMB +H_2O_2 + Nanozyme (on magnetic field) (right))

3.1.2. 4-nitrophenol reduction

The use of the synthesized composite is not limited to just colorimetric detection of H_2O_2. The catalytic degradation 4-nitrophenol at the presence of $NaBH_4$ using the synthesized composite was explored. Although $NaBH_4$ is a strong reductant, it is unable to degrade 4-nitrophenol over a reasonable period of time[24]. However, with the introduction of Fe_3O_4@MIL-100(Fe)-Au into the reaction system, the degradation of 4-nitrophenol is effected as shown in Figure 5a. Furthermore, an enhanced rate of degradation was observed when the catalysis was executed on a magnetic field as presented in Figure 5b.

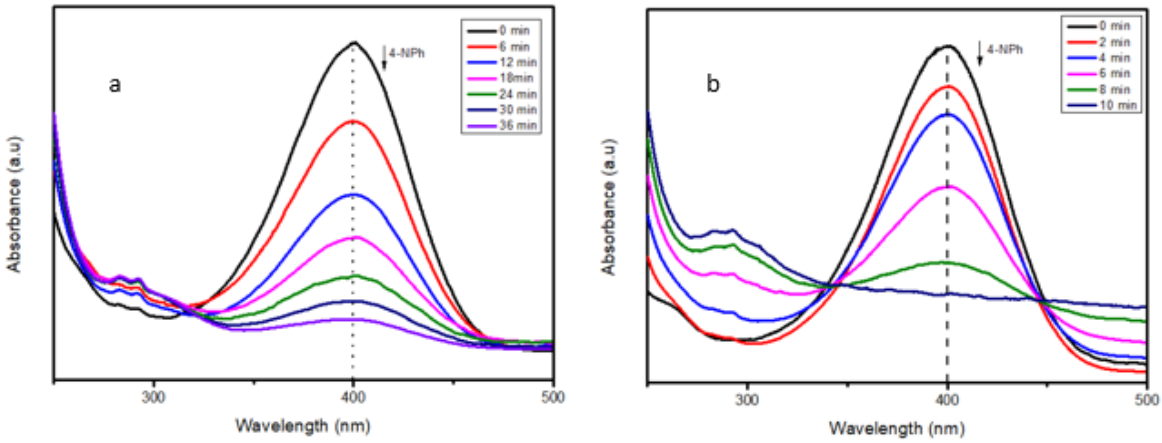

Figure 5. UV-vis spectra for a) Non-magnetic field-assisted catalysis of 4-nitrophenol b) Magnetic field-assisted catalysis of 4-nitrophenol.

3.2.3. Bacteria adsorption

The magnetic property of exhibited by the composite was also utilized to enhance the capture of bacteria pathogen. After the composite was conjugated with antibodies of salmonella, the adsorption of salmonella pathogen was more enhanced for magnetic field-assisted adsorption as compared to the non-magnetic field-assisted adsorption (Figure 6 a and b). This observation also highlights the importance of the magnetic property of the composite.

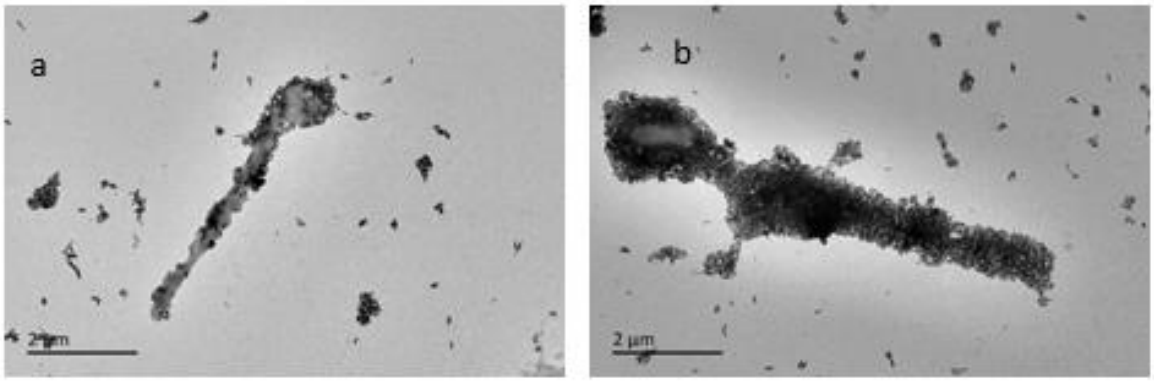

Figure 6. TEM of bacteria pathogen adsorption a) In the absence of magnetic field b) Magnetic field-assisted system.

5. Conclusions

In conclusion, rod-based magnetite MOF- metal composite was successfully synthesized and utilized for the colorimetric detection of the green oxidant, H_2O_2. The magnetic property of the composite was further harnessed to enhance the rate of detection of H_2O_2. Besides, the versatility of Fe_3O_4@MIL-100(Fe)-Au was demonstrated by successfully applying the composite for the catalytic reduction of 4-nitrophenol and for the adsorption of bacteria pathogen. In all cases, the magnetic property was utilized to enhance the kinetics of catalysis and adsorption.

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