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COMMUNICATION

Facile synthesis of Fe₃O₄/MIL-101(Fe) composite with enhanced catalytic performance

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A magnetic porous material $Fe_3O_4/MIL-101(Fe)$ has been successfully fabricated by using a simple ultrasound-assisted electrostatic self-assembly technology, which was demonstrated to be an highly active heterogeneous catalyst for the dimerization reaction of *o*-phenylenediamine (OPD) in the presence of H_2O_2 via a synergistic peroxidase-like activity.

Metal-organic frameworks (MOFs), as well-known as a new class of porous materials, synthesized by assembling with metal cations/clusters and organic linkers have attracted significant research interest in recent years,1 not only for the diversiform topological structure but also for their many attractive applications in adsorption and separation², sensing³, drug delivery⁴ and catalysis⁵. Recently, Fe-based MOFs have been widely used in catalytic applications due to the catalytically active coordinatively unsaturated Fe (III) sites and the existence of Fe₃- μ_3 -oxo clusters which endows iron-containing MOFs photocatalytic activity.⁶ Moreover, intrinsic peroxidase-like activity, a new performance of Fe-based MOFs which shows ability of catalytic decomposition of hydrogen peroxide (H₂O₂) to •OH radicals via a Fenton-like route has been found recently and it shows a wide range of applications in biosensing platform.⁷ As far as we know, there was no report about that the catalytic performance towards the organic synthesis by utilizing the peroxidase-like activity of Fe-based MOFs.

Magnetic nanoparticles (MNPs) have received considerable attention because of their power in separation techniques. Among various magnetic particles, iron oxides (such as Fe_3O_4 MNPs) have drawn the most attention owing to their strong magnetic responsiveness and biocompatibility. As magnetic separation is directly performed on complex samples, the functionalized Fe_3O_4 MNPs are usually used for the preconcentration and isolation of analytes from complex matrices.⁸ For instance, MNPs have been used for separating DNA, proteins, cells from samples⁹ and catalyst

recycling in organic synthesis aspect¹⁰. In addition, a research reported that Fe_3O_4 MNPs exhibit peroxidase-like activity allowing the effective detection of H_2O_2 .¹¹ Since then, Fe_3O_4 MNPs pose the widespread applications in sensing and water purification by utilizing the peroxidase-like activity.¹²

Controllable integration of MOFs and functional materials is resulting in the creation of new multifunctional composites, which exhibit new properties that are superior to those of the individual components through the collective behavior of the functional units.¹³ For the magnetization of MOFs, five different synthesis approaches, including, hydrothermal¹⁴, encapsulation¹⁵, *in-situ* magnetization¹⁶, chemical bonding¹⁷ and coprecipitation assembly¹⁸ were attempted by previous report. Wherein, the magnetized MOFs were used for catalysis, extraction and separation. Intriguing by these meaningful researches and given the tremendous emerging interest in this field, we present an ultrasound-assisted electrostatic self-assembly strategy that has allowed us to rationally design and fabricate a novel type of magnetic composites in a general approach.

In our strategy, MIL-101 (Fe), a kind of Fe-based MOFs, was chose as a matrix for loading Fe₃O₄ MNPs due to the outstanding peroxidase-like activity among the reported Fe-based MOFs owing to the high BET surface, mesosize cages and superior affinity for H₂O₂.¹⁹ Typically, cysteine (Cys) functionalized Fe₃O₄ MNPs and MIL-101(Fe) suspensions were mixed together under ultrasonication at room temperature for 10 minutes and the magnetic composite would be obtained by magnetic separation. The Fe₃O₄/MIL-101(Fe) magnetic composite prepared by this method displays high saturation magnetization value, making this composite more susceptible to magnetic fields and easier to isolate from aqueous solution. Furthermore, the as-synthesized Fe₃O₄/MIL-101(Fe) exhibits much higher catalytic activity than the single component for the synthesis of 2,3-diaminophenazine (2,3-DPA) due to the synergistic peroxidase-like activity between the multiple active centers, including Fe₃O₄ MNPs and MIL-101(Fe), which improved the decomposition efficiency of H₂O₂ and produced abundant reactive oxygen species (ROS) (Scheme.1).

Powder XRD patterns of the parent materials (MIL-101(Fe), Fe₃O₄) and the hybrid Fe₃O₄/MIL-101(Fe) are shown in Fig. 1A. The diffraction peaks of MIL-101(Fe) and Fe₃O₄ are observed in the PXRD patterns of the as-synthesized hybrid Fe₃O₄/MIL-101(Fe), which confirms that the MIL-101(Fe) represented the major

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Scheme.1 Schematic illustration of the synergistic catalytic behavior of $Fe_3O_4/MIL-101(Fe)$ for the oxidation of OPD.

component of the composite, and it also indicated that the hybrid $Fe_3O_4/MIL-101(Fe)$ preserved the crystalline characters of parent MIL-101(Fe). The diffraction intensity of Fe_3O_4 in the PXRD patterns of $Fe_3O_4/MIL-101(Fe)$ was relatively weak, probably because the low content of Fe_3O_4 in the composite. The Brunauer–Emmett–Teller (BET) surface area of the as-synthesized MIL-101(Fe) and $Fe_3O_4/MIL-101(Fe)$ were evaluated by nitrogen adsorption-desorption isotherms (Fig. 1B). The BET surface area of the naked MIL-101 and the hybrid $Fe_3O_4/MIL-101(Fe)$ are calculated to be $1362 \text{ m}^2/\text{g}$ and $1248 \text{ m}^2/\text{g}$, respectively. Obviously, $Fe_3O_4/MIL-101(Fe)$ still maintained a high specific surface area although the BET surface area of MIL-101(Fe) is minor higher than that of $Fe_3O_4/MIL-101(Fe)$. Besides, the pore size of $Fe_3O_4/MIL-101(Fe)$ is similar to that of MIL-101(Fe) with a little change (Fig. S1).



Fig.1 The characterization of $Fe_3O_4/MIL-101(Fe)$.(A) PXRD pattern of MIL-101(Fe), Fe_3O_4 and $Fe_3O_4/MIL-101(Fe)$; (B) The N₂ adsorption-desorption isotherms of MIL-101(Fe) and $Fe_3O_4/MIL-101(Fe)$; (C) The hysteresis loop of Fe_3O_4 and $Fe_3O_4/MIL-101(Fe)$; (D) SEM images of $Fe_3O_4/MIL-101(Fe)$.

In addition, the magnetization curve illustrates the superparamagnetic characteristic of Fe_3O_4 and $Fe_3O_4/MIL-101(Fe)$ (Fig. 1C). The saturation magnetization values were measured to be 50 emu/g and 23 emu/g respectively, which is susceptible to magnetic fields and easy to isolate from aqueous solution. The photographs of dispersed MIL-101(Fe) and $Fe_3O_4/MIL-101(Fe)$ are shown in Fig. S 2A and B, respectively. A clear solution could be obtained after separation of $Fe_3O_4/MIL-101(Fe)$ by using the external magnet in 20 s (Fig. S2C). In order to better understand the

morphological structure of the hybrid material Fe_3O_4 /MIL-101(Fe), the texture of the samples were observed by scanning electron microscope (SEM). As can be seen from Fig. 1D, the surface of MIL-101(Fe) with a particle size of 1.1 µm has been successfully decorated with Fe_3O_4 nanoparticles without any influence on the morphology of MIL-101(Fe). The transmission electron microscope (TEM) images also demonstrated that the Fe_3O_4 MNPs with particle size about 10 nm were attached on the surface of MIL-101(Fe) successfully (Fig. S3).

As we know, Cys is a kind of ampholyte with an isoelectric point of 5.05. Therefore, the prepared Cys-functionalized Fe₃O₄ MNPs should exhibit different zeta potential under various pH of the suspension. The as-prepared MIL-101(Fe) shows a strong electropositive. Hence, in order to obtain electronegative Fe₃O₄ MNPs, the pH of the suspension has been tuned from 6.0 to 10.0 (Fig. 2A). With the increase of the pH, the electronegativity of Cys-Fe₃O₄ become stronger and the corresponding electropositivity of the as-prepared Fe₃O₄/MIL-101(Fe) get weaker. Unfortunately, when the pH of Cys-Fe₃O₄ MNPs suspension was tuned to 10.0, the assynthesized Fe₃O₄/MIL-101(Fe) would aggregate seriously. So, the pH of Cys-Fe₃O₄ MNPs suspension was selected as 9.0 with the purpose of obtaining stable dispersion of Fe₃O₄/MIL-101(Fe). As shown in Fig. 2B, the zeta potential of Cys-Fe₃O₄MNPs is -36.87 mV at pH of 9.0, and 35.37 mV for that of original MIL-101(Fe) suspension. The corresponding Fe₃O₄/MIL-101(Fe) shows weak electropositivity (11.23 mV) without obvious aggregation.



Fig. 2 (A) Zeta potential of Fe_3O_4 and the corresponding $Fe_3O_4/MIL-101(Fe)$ under various pH; (B) the changes of zeta potential before and after reaction.

Liquid-phase dimerization reaction of OPD to 2,3-DPA in the presence of H₂O₂ was used as a model reaction system to characterize the catalytic performance of the Fe₃O₄/MIL-101(Fe). When the Fe₃O₄/MIL-101(Fe) catalyst was introduced into the solution, the fluorescence of 2,3-DPA increased along with the time's going and showed an intensive yellow-green fluorescence under UV excitation (Fig. S4). The product 2,3-DPA shows a strong fluorescence emission (558 nm) in methanol under 439 nm excitation. So, the reaction process was monitored by fluorescence standard curve method (Fig. S5). The standard curve has a good linear relationship $(R^2=0.998)$ with a linear equation y=24.60c+37.52. The reaction proceeds slowly over the Cys-Fe₃O₄ MNPs and MIL-101(Fe) catalysts, while the catalytic activity of the Fe₃O₄/MIL-101(Fe) catalyst is noticeably better under the same conditions (Fig. 3). It also indicated that the catalytic efficiency of H₂O₂ is very low without Fe₃O₄/MIL-101(Fe). The possible reaction mechanism was shown in Fig.S6. The Fe₃O₄/MIL-101(Fe) shows excellent catalytic activity for the decomposition of H2O2 and produces abundant reactive oxygen species (ROS) which was involved in the whole oxidation of OPD.

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Fig. 3 Catalytic conversion of OPD to 2,3-DPA over Cys-Fe₃O₄ MNPs, MIL-101(Fe) and Fe₃O₄/MIL-101(Fe), respectively.

Similar to peroxidase, the catalytic activity of Fe_3O_4 /MIL-101(Fe) was found to be closely dependent on pH, temperature, H_2O_2 concentration, and so on. Therefore, the reaction conditions, such as the concentration of H_2O_2 and Fe_3O_4 /MIL-101(Fe), pH, temperature, and reaction time, have been optimized (Fig. S7). Under the optimal reaction conditions, the Fe_3O_4 /MIL-101(Fe) displayed a higher catalytic activity than that of Cys-Fe₃O₄ MNPs and MIL-101(Fe), achieving 97.79% yield of 2,3-DPA(Fig. S8). Compared with other existing catalyst (Table S1), the as-synthesized Fe_3O_4 /MIL-101(Fe) shows highest catalytic efficiency among the reported catalyst for the oxidation of OPD. For the product 2,3-DPA (structure displayed in Fig. S9), the characterization data of FTIR, ¹H NMR, ¹³C NMR and ESI-TOFMS are showed in Fig. S10-13, respectively.

From the results shown above, one can easily draw a conclusion that the catalytic activity of Fe₃O₄/MIL-101(Fe) is higher than those of Cys-Fe₃O₄MNPs and MIL-101(Fe) for the same reaction time. This catalytic activity enhancement can be attributed to the synergistic effect of Cys-Fe₃O₄MNPs and MIL-101(Fe). Furthermore, the recyclability of the Fe₃O₄/MIL-101(Fe) catalyst was also examined in the dimerization reaction of OPD. The catalyst was isolated by magnetic separation from the reaction mixture and washed with methanol, and reused for the next run under the same conditions. The results indicated that no significant loss of activity for the dimerization reaction of OPD was observed over Fe₃O₄/MIL-101(Fe) in the five successive catalytic cycles, suggesting that the Fe₃O₄/MIL-101(Fe) possesses long-term stability (Fig. 4). The atomic absorption spectrometry (AAS) has been used for monitoring the leaching test. The total iron content which leached from the composite would have a relatively high leaching quantity in the firsttime using. The highest leaching amount is 1.153 ng/mL. The leaching amount dropped dramatically with the increase of cycling times, and even no iron was detected after three cycles (Fig.S14). However, the catalytic efficiency of the composite is still maintained at a high level. It indicates that the catalytic activity is mainly derived from the composite material rather than the leached iron ion. After five recycling use, the PXRD pattern showed that the used Fe₃O₄/MIL-101(Fe) keeps close to the originality (Fig. S15). As can be seen from the X-ray photoelectron spectroscopy (XPS) spectrums (Fig.S16), there were no changes between the fresh and recovered $Fe_3O_4/MIL-101(Fe)$. It indicates that the composite remains the integrity without any valence state change before and after the reaction. Besides, the morphology of Fe₃O₄/MIL-101(Fe) has no serious changes and no great influence upon the catalytic activity after five consecutive reaction cycles (Fig. S17).



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Fig. 4 The productivity of 2,3-DPA using Fe₃O₄/MIL-101(Fe) as catalyst after five consecutive reaction.

In summary, we have developed a facile, general and effective ultrasound-assisted electrostatic self-assembly strategy for immobilizing Fe_3O_4 MNPs on the surface of MIL-101(Fe). The catalytic property of Fe_3O_4 /MIL-101(Fe) was evaluated by using the dimerization reaction of OPD as a model reaction system. It is noteworthy that the as-prepared Fe_3O_4 /MIL-101(Fe) composite synergistically improves the catalytic activity compared to the Cys- Fe_3O_4 and MIL-101(Fe). Furthermore, the high catalytic activity was retained after a number of reaction cycles with a slightly change. This study may bring light to new opportunities in the development of high performance heterogeneous catalysts based on the peroxidase-like activity of Fe-based MOFs or nanostructures.

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The as-prepared Fe₃O₄/MIL-101(Fe) shows enhanced catalytic performance for dimerization reaction of *o*-phenylenediamine *via* a synergistic peroxidase-like activity.