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The use of g-C$_3$N$_4$/MOFs(Fe) as a photocatalyst for remediation of pharmaceutics in water

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Abstract

Metal-organic framework MIL-101(Fe) was deposited successfully on g-C$_3$N$_4$ templates under solvothermal treatment. The results of XRD, FT-IR, and SEM measurements revealed the growth of MIL-101(Fe) crystals on g-C$_3$N$_4$ to fabricate the g-C$_3$N$_4$/MIL-101(Fe) hybrid. The photocatalytic ability of g-C$_3$N$_4$/MIL-101(Fe) was examined through the photodegradation performance of paracetamol in an aqueous solution under visible light irradiation. Among the samples, 0.5CN-M, standing for 0.5 g of g-C$_3$N$_4$ used for fabrication of g-C$_3$N$_4$/MIL-101(Fe), showed the best photocatalytic ability when degraded about 34% of paracetamol in water. The effective photocatalytic performance of g-C$_3$N$_4$/MIL-101(Fe) than that of MIL-101(Fe) might result from the high surface area of MIL-101(Fe) and the formation of heterojunction layer between this MOF and g-C$_3$N$_4$.

1. Introduction

The harm of pharmaceutical waste in water has been a global concern for a long time, due to its negative influences on the environment and ineffective conventional methods of removal of these compounds as well. Going with the effort to reduce pharmaceuticals released into the environment, many strategies to inhibit their unwanted effects were taken place, including sorption, chemical advance oxidation, dilution, or biological degradation [1]. Two promising methods are adsorption on solid matters and photocatalytic degradations. For the adsorption method, traditional adsorbents can be listed as activated carbon, zeolites, and clays [2]. However, the adsorption process takes place only on the surface of solid materials, thus limiting the removal efficiency of organic compounds. Photocatalysis is considered a more effective solution when organic compounds can be degraded by light-generated radicals in water. Typical inorganic semiconductors such as TiO$_2$, ZnO, Fe$_2$O$_3$, and BiVO$_4$ can be mentioned as representatives, thanks to their high stability, availability, and low cost. However, their drawbacks are high agglomeration, low surface area, and activation under a narrow range of solar light [3, 4].

Metal-organic frameworks (MOFs) are highly porous crystalline materials constructed of metal ions and multifunctional organic ligands via coordination bonds, forming unlimited networks containing different pore sizes and shapes of windows. The potentials of MOFs were investigated in many fields, including gas sorption and separation, catalysis, and drug delivery, because of their variety and adjustability of structures and compositions [5]. For removal of harmful chemicals in water, MOFs were considered a promising alternative material that showed many unique properties, such as high porosity, large surface area, well-defined crystal lattice, and ability to harvest photons in a wide range of solar spectra, which increase the efficiency of sorption and degradation processes [6, 7].

Among MOFs, MIL-101(Fe) (MIL standing for Materials Institute Lavoisier) has shown a highly porous structure, large surface area, and high stability in water. The stability of MIL-101(Fe) is because of coordination bonds between high-valence Fe(III) and carboxylate groups stabilizing the MOF structure under the appearance

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of water molecules, rationalized by the hard-soft acid-base principle [8]. Therefore, the use of MIL-101(Fe) as a photocatalyst for the degradation of pharmaceuticals in water has been examined, but the efficiency was still lower than expected. Fabricating a hybrid system of different semiconductors, in which the lifetime of light-driven free charges on the surface of materials increases, is an effective strategy to improve photocatalytic efficiency. So, the fabrication of MOF-based hybrids, especially with inorganic semiconductors, is a considerable solution to enhance the degradation efficiency of pharmaceuticals.

Graphitic carbon nitride g-C₃N₄ is a free-metal compound having a similar structure to graphene and presenting interesting physicochemical properties, including high thermal and chemical stability [9]. Activated under visible light irradiation, g-C₃N₄ itself exhibited photocatalytic ability for water splitting activity, degradation of RhB, and NO removal. Even though, the photocatalytic ability of g-C₃N₄ is still low due to the fast recombination of light-driven charges [10].

In this research, we synthesized g-C₃N₄/MIL-101(Fe) for photodegradation of paracetamol, a residual pharmaceutical compound commonly present in water bodies. The high porosity of MIL-101(Fe) combining the high stability of g-C₃N₄ is expected to enhance the photocatalytic efficiency of paracetamol removal.

2. Material and methods

Iron (III) chloride (FeCl₃, 6H₂O, >98%) and N,N-Dimethylformamide (DMF, >99%) from Aldrich, Benzene-1,4-dicarboxylic acid (H₂BDC: C₆H₄(COOH)₂, >98%) from Junsei, Urea ((NH₄)₂CO, >99%), Ethanol (C₂H₅OH, 99.9%) from Duc Giang, and other chemicals were analytical grade and used without further purification. Deionized water was used where needed.

**Synthesis of MIL-101(Fe):** MIL-101(Fe) was synthesized via the solvothermal method according to a previous report [11] with some modifications. Briefly, H₂BDC and FeCl₃.6H₂O (1:1 in mole) were dissolved one by one in 50 ml of DMF and stirred until forming a transparent solution. The solution was transferred to a Teflon-core vessel and then heated in an oven under 150 °C for 24 h. The obtained powder was centrifuged and washed with various solvents including DMF, ethanol, and doubly distilled water, then dried in an oven at 80 °C for 12 h and stored in a vacuum box.

**Synthesis of g-C₃N₄ and g-C₃N₄/MIL-101(Fe):** Graphitic carbon nitride was prepared by heating urea powder in a muffle furnace under 450 °C (heating rate of 10 °C min⁻¹) for 4 h. The obtained yellow sample was ground and stored in the vacuum box.

The hybrid system of g-C₃N₄/MIL-101(Fe) was fabricated via the solvothermal method. In detail, a 50 ml DMF solution of FeCl₃ and H₂BDC (1:1 in mole) was prepared, then a different amount of as-synthesized g-C₃N₄ was dispersed with 30 min of sonication. After solvothermal preparation at 150 °C for 24 h, the solid sample was collected and cleaned using a similar procedure to that of MIL-101(Fe).

**Materials characterization:** The products were identified by x-ray diffraction analysis using D/Max, 2200HR, Rigaku, Japan, with Cu Kα radiation (λ = 1.54 Å). A scanning electron microscope (SEM, JEOL-2020) was used to evaluate the morphology and particle size of samples. The photoresponse ability of the samples was established by a UV–vis diffuse reflectance spectrophotometer (NIR JASCO 570). The surface area of the samples was evaluated by the Brunauer-Emmett-Teller theory by nitrogen gas absorption-desorption method using Micromeritics ASAP 2020 system. All samples were degassed for at least 12 h under at 150 °C vacuum conditions, N₂ adsorption-desorption isotherms were measured at 77K.

**Photocatalytic activity tests:** In a typical photodegradation experiment, 50 mg of the sample powder was dispersed in 50 ml of an aqueous solution of paracetamol (10 mg.L⁻¹). Before irradiation, the solution was strongly stirred in the dark for 30 min to obtain absorption-desorption equilibrium between the organic substrate and the catalyst surface. A 75 W LED lamp with a UV cut-off (< 400 nm) was used as a visible light source for photocatalysis. At each time of period selected, aliquots of the solution were collected, centrifuged, and filtered by membranes to remove the catalyst particulates. The concentration of the rest of the solution was evaluated using a Thermo HPLC series 1100 with a Thermo-C18 column (5 mm, 4.6250 mm) with solvent A (100% water) and solvent B (acetonitrile ACN).

3. Results and discussion

The crystallinity of as-synthesized samples was confirmed by XRD results (figure 1).

For the MIL-101(Fe) sample, the characteristic peaks at 2.9°, 3.2°, 6.1°, 8.7°, 9.1° confirmed the successful synthesis of MIL-101(Fe) with high purity [12]. The high intensity of these peaks on XRD patterns indicated the good crystallinity of the MOF(Fe). In comparison, the samples of 0.2CN-M and 0.5CN-M, containing 0.2 g and 0.5 g of g-C₃N₄ respectively, showed lower crystallinity. On the XRD patterns of such two samples, the characteristic peaks of MIL-101(Fe) still appeared but showed lower intensity. Particularly, these peaks did not
appear on XRD patterns of 1.0CN-M prepared by adding 1.0 g of g-C3N4. Only a board peak observed at 27° of 2θ was attributed to the (002) plane of g-C3N4, which was hardly observed on XRD patterns of 0.2CN-M and 0.5CN-M [13]. Indeed, the results of XRD proved the association of MIL(Fe) and g-C3N4 in the hybrid samples but in 1.0CN-M samples.

To further confirm the formation of g-C3N4/MIL-101(Fe), FT-IR spectra of as-synthesized samples were recorded and illustrated in figure 2. In the IR spectrum of g-C3N4, the absorption bands ranging from 1600 to 1200 cm\(^{-1}\) originated from aromatic C-N stretching mode, and the band at 1639 cm\(^{-1}\) can be assigned to C = N stretching mode. The sharp band at 810 cm\(^{-1}\) might belong to the breathing mode of triazine units [13]. In IR spectra of g-C3N4/MIL-101(Fe), the absorption bands of g-C3N4 also appeared with absorption bands corresponding to characteristic groups in MIL-101(Fe). Even though the absorption bands of MIL-101(Fe) almost overtopped those of g-C3N4, IR spectra again proved the co-existence of MIL(Fe) and g-C3N4 in the synthesized samples.

The morphology of all the samples was observed by using SEM images, as presented in figures 3(a)–(e). Herein, MIL-101(Fe) showed regular particle size at a range of hundreds of nanometers, whereas bulk g-C3N4 showed inhomogeneous morphology with a large amount of agglomerated thin layers. For hybrid samples, MIL-101(Fe) grew and tended to aggregate on g-C3N4 sheets, resulting from the agglomerated
structure of g-C₃N₄. SEM images revealed that MIL-101(Fe) particles remained in size and octahedral shapes when decorating on g-C₃N₄, verifying that adding g-C₃N₄ to the solution of precursors of MIL-101(Fe) did not alter the morphology of the MOF. As shown in SEM images of three hybrid samples, when increasing g-C₃N₄ composition to the solution of precursors, the ratio of MIL-101(Fe) attached to g-C₃N₄ decreased. For the 1.0CN-M sample, only very few MIL-101(Fe) particles on g-C₃N₄ presented, which might be due to the high concentration of g-C₃N₄ in the solution inhibited the formation of crystalline nuclei of MIL-101(Fe). The SEM images also matched to results obtained from XRD patterns in which the characteristic peaks of MIL-101(Fe) hardly appeared for the 1.0CN-M sample.

Specific surface area strongly influences the efficiency of adsorption and photocatalysis ability of a material, so the porosity of g-C₃N₄ and as-synthesized hybrid samples were investigated by nitrogen sorption technique, and the surface area of them was calculated via BET method, as presented in figure 4.

The nitrogen sorption isotherms of all samples were of type IV with H4 hysteresis loops at a range from 0.9–1.0 of relative pressure, showing the association of mesopores and micropores of the samples. Particularly, the secondary uptakes at low relative pressure in the 0.5CN-M’s isotherm indicated the presence of two kinds of micropores, which was similar to MIL-101(Fe) [14]. Among the samples, g-C₃N₄ has the lowest surface area at
24 m² g⁻¹, due to its high agglomerated structure. In comparison, g-C₃N₄/MIL-101(Fe) samples obtained a much higher surface area, from 156 to 356 m² g⁻¹, resulting from the integration of high porous MIL-101(Fe). Noteworthy, the surface area of the materials did not decline when increasing the amount of g-C₃N₄ but obtained the highest value in the case of the 0.5CN-M sample. An assumption is that a large amount of g-C₃N₄ might inhibit the formation of MOF nuclei, while a small amount of g-C₃N₄ might not supply enough surface for MIL-101(Fe) particles to attach and develop, by contract. For the 0.2CN-M sample, the aggregation of MIL-101 particles on a small area of g-C₃N₄ substrates thus led to a lower surface area than that of the 0.5CN-M sample.

To examine photoresponsivity properties of as-synthesized samples, UV–vis diffuse reflectance spectroscopic was carried out and the spectra have shown in figure 5. Herein, absorption spectra have shown the light-absorption range of pristine g-C₃N₄ from 200 to 500 nm, indicating that g-C₃N₄ can be activated under UV light or blue light irradiation. In comparison, absorption spectra of MIL-101(Fe) prolonged to 650 nm, so MIL-101(Fe) can absorb photons in a wider range of visible light. The prolongation was also observed in the case of hybrid samples, the intensity of the absorption peak at 450–600 nm assigned to the charge transfer in Fe-O clusters of MOFs decreased when increasing the amount of added g-C₃N₄. This might be due to the cover of g-C₃N₄ sheets on MIL-101(Fe) and the high aggregation of MIL-101(Fe) particles in the hybrid samples. Consequently, the peak intensity of 0.2CN-M and 0.5CN-M samples were slightly lower than that of MIL-101(Fe), whereas the peak intensity of 1.0CN-M was similar to g-C₃N₄.

To investigate the stability of the hybrid samples, MIL-101(Fe) and 0.5CN-M were dispersed in distilled water and kept for hours. After that, the solid powders were re-collected, dried for at least 12h and evaluated via XRD to confirm the structure (figure 6). After 4 h in an aqueous environment, identical peaks of MIL-101(Fe) disappeared, indicating the collapse of MIL-101(Fe) structure. Meanwhile, the characteristic peaks of MIL-101(Fe) phase and g-C₃N₄ phase of 0.5CN-M still presented after 4h in water. The decrease of the peak intensity of MIL-101(Fe) phase and the slight increase of that of g-C₃N₄ phase evidenced that MIL-101(Fe) partly decomposed from the hybrid sample. Even though most of these peaks disappeared when 0.5CN-M was in the water for 8 h, the stability of the hybrid g-C₃N₄/MIL-101(Fe) in water was higher than pristine MIL-101(Fe).

To assess the photocatalytic ability of g-C₃N₄/MIL-101(Fe), the photodegradation of paracetamol was conducted under visible light irradiation using the prepared samples as photocatalysts, the result was described in figure 7. The adsorption–desorption equilibrium of all samples was obtained after 30 min in dark. Dispersed in an aqueous solution with 1 mg L⁻¹ of photocatalyst concentration, 1.0CN-M samples obtained the fastest equilibrium after 10 min but only adsorbed about 4% of paracetamol. Meanwhile, 0.2CN-M adsorbed about 7% of paracetamol, MIL-101(Fe) and 0.5CN-M have shown the highest adsorption efficiency when removed about 14% and 10%, respectively, of the target compound from the solution. The difference in adsorption ability of the samples results from the difference in surface area which was confirmed by BET result. The adsorption efficiency of all the samples was still low, due to the large scale of paracetamol molecules that inhibited the deep
penetration of this compound into the material pores, so reducing the interaction between the adsorbent and adsorbate.

For the photocatalytic process, only 12% of paracetamol degraded after 120 min irradiation when using MIL-101(Fe) photocatalyst even though this MOF adsorbed 11% of the organic compound. Two samples that obtained the highest photocatalytic efficiency were 0.2CN-M and 0.5CN-M, those degraded 31% and 34% of paracetamol, respectively. For the 1.0CN-M sample, 13% of paracetamol photodegraded after 120 min irradiation, demonstrating that adsorption capability did not guarantee a higher photocatalytic efficiency. Indeed, all the g-C3N4/MIL-101(Fe) exhibited a higher photocatalytic ability than MIL-101(Fe) though the single MOF adsorbed paracetamol the most. Compared to MOF-containing samples, g-C3N4 showed the lowest adsorption efficiency, and also degraded was 25% of paracetamol, which was lower than 0.2CN-M and 0.5CN-M but higher than MIL-101(Fe) and 1.0CN-M. This might be due to the bulk form and hydrophobic nature of this material. Compared to the hybrid samples, MIL-101(Fe) had a higher surface area [15], increasing the interaction of the MOF and paracetamol molecules, thus leading to improving the adsorption capability. However, the high concentration of paracetamol on MIL-101(Fe) might cover the active centers of the MOF and prevent the photon absorption process, thus reducing the photocatalytic efficiency. Moreover, the appearance of

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**Figure 6.** XRD patterns of MIL-101(Fe) and 0.5CN-M after hours dispersed in water.

**Figure 7.** Photocatalytic degradation of paracetamol under visible light irradiation using MIL-101(Fe) and g-C3N4/MIL-101(Fe) as photocatalysts.
a larger number of mesopores on g-C₃N₄/MIL-101(Fe) (figure 4) enhanced the transfer of organic molecules between the solution and the solid sample’s surface. The lowest photocatalytic ability of MIL-101(Fe) might result from the fast recombination of photon-induced charges as well. Therefore, the formation of heterojunction between MIL-110(Fe) and g-C₃N₄ helps to extend the lifetime of electron-hole pairs, leading to increasing the photocatalytic ability of the material. Among the hybrid samples, 0.5CN-M exhibited the highest photocatalytic ability, as a result of a high surface area, well photon harvesting, and a better adsorption capability than other samples.

4. Conclusion

In this work, g-C₃N₄/MIL-101(Fe) was successfully synthesized by a solvothermal method when MIL-101(Fe) crystals were deposited on g-C₃N₄ without collapsing the MOF network. The photocatalytic ability of as-synthesized samples has been evaluated through the photodegradation of paracetamol under visible light irradiation. Among them, the 0.5CN-M sample expressed the highest photocatalytic ability when removed 34% of paracetamol from an aqueous solution under 120 min of visible light irradiation. The growth of MIL-101(Fe) on the g-C₃N₄ substrate has changed MOF particle distribution and the specific surface area of the material, and also formed the heterojunction interface between MIL-101(Fe) and g-C₃N₄, all of which contributed to enhancing the efficiency of organic pollutants removal. The improvement of the photocatalytic ability of MOF-based materials thus might be a better strategy for the removal of pharmaceutical pollutants than the adsorption method when it can manage the limitation of adsorption saturation.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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