



A Highly Efficient Composite Catalyst Constructed From NH₂-MIL-125(Ti) and Reduced Graphene Oxide for CO₂ Photoreduction

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Specialty section:

This article was submitted to
Catalysis and Photocatalysis,
a section of the journal
Frontiers in Chemistry

Received: 06 August 2019

Accepted: 01 November 2019

Published: 15 November 2019

Citation:

Zhao Y, Cai W, Chen J, Miao Y and
Bu Y (2019) A Highly Efficient
Composite Catalyst Constructed
From NH₂-MIL-125(Ti) and Reduced
Graphene Oxide for CO₂
Photoreduction. *Front. Chem.* 7:789.
doi: 10.3389/fchem.2019.00789

Substantial consumption of fossil fuels causes an increase in CO₂ emissions and intensifies global pollution problems, such as the greenhouse effect. Recently, a new type of ultra-low-density porous material, metal-organic frameworks (MOFs), has been developed for the photocatalytic conversion of CO₂. Herein, a composite photocatalytic catalyst based on NH₂-MIL-125(Ti) and reduced graphene oxide (rGO@NH₂-MIL-125) was fabricated through a facile “one-pot” process. The acquired materials were characterized to obtain their structures, morphologies, and optical information. The experimental results showed that methyl formate (MF) was the predominant reaction product, and rGO@NH₂-MIL-125 exhibited the highest yield of 1,116 μmol·g⁻¹·h⁻¹, more than twice that of pure MIL-125. The high photoactivity of rGO@NH₂-MIL-125 can be ascribed to the effective spatial separation and transfer of photoinduced carriers, largely due to the synergistic effect of amino functionality and rGO incorporation. rGO@NH₂-MIL-125 also displayed acceptable repeatability in cyclic runs for CO₂ reduction.

Keywords: CO₂ reduction, photocatalysis, metal-organic frameworks (MOFs), reduced graphene oxide, methyl formate

HIGHLIGHTS

- The agglomerate state of NH₂-MIL-125(Ti) was improved by introducing reduced graphene oxide.
- The composite catalyst could efficiently enhance photogenerated charge separation.
- The composite photocatalyst showed effective activity in reducing CO₂ in CH₃OH to HCOOCH₃.
- The composite catalyst exhibited acceptable stability in cyclic runs for CO₂ reduction.

INTRODUCTION

With the economic and social development, the CO₂ concentration in the atmosphere is increasing, causing global warming, and other climate problems. CO₂ emissions mainly come from mobile or immobile sources (e.g., vehicles and coal power plants). The reduction of CO₂ emissions is essential to address the global issue of climate change. Both the capture and sequestration technology of

CO₂ (Anwar et al., 2018; Luis Míguez et al., 2018) and the chemical conversion of captured CO₂ into useful chemicals or clean fuels using solar energy (Fu et al., 2018; Lee et al., 2018; Wang et al., 2018a) at normal temperatures and pressures are promising approaches that can simultaneously solve two problems by addressing global environmental pollution and energy deficiency.

Photocatalytic CO₂ reduction is one CO₂ conversion technology, and its key lies in the catalyst. In 1979, Inoue et al. (1979) synthesized semiconductor TiO₂ as a catalyst for photoirradiation of the CO₂ reduction reaction in an aqueous solution filled with CO₂. The reduction products, CH₂O, HCOOH, CH₃OH and CH₄, were obtained, and this result laid the foundation for photocatalytic CO₂ reduction. Thereafter, TiO₂ was continuously proven to be an efficient and promising photocatalyst (Liu G., et al., 2018; Wang et al., 2018b, 2019). Various Ti-based modified catalysts have been designed and developed for improving the CO₂ photoreduction efficiency (Jiang et al., 2018; Zhao et al., 2018). It was found that an appropriate bandgap width and band structure, good electron-hole separation performance, and abundant reaction active sites favor excellent photocatalytic efficiency (Usubharatana et al., 2006; Crake et al., 2017). Metal-organic frameworks (MOFs) are one type of porous material with ordered crystal structures constructed from metal nodes (metal ions) and organic linkers (Millward and Yaghi, 2005). In recent years, research on MOFs has spread to the catalysis and CO₂ conversion fields (Crake et al., 2017; Fang et al., 2018; Li et al., 2018a; Zhang et al., 2018). Ti-based MOFs are considered promising candidates for CO₂ photocatalytic reduction (Sun et al., 2014; Li et al., 2018a; Zhang et al., 2018) because their Ti-O clusters can be regarded as isolated titanium oxide quantum dots (Sun and Li, 2017). Fu et al. (2012) and Li et al. (2018a) studied the photocatalytic CO₂ reduction performance on MIL-125(Ti). After 10 h of UV-light irradiation, 2.41 μmol HCOO⁻ was detected in the acetonitrile (MeCN) solvent with triethanolamine (TEOA). Then, amino-functionalized MIL-125 was also investigated for CO₂ photoreduction, and a possible mechanism for this photocatalysis reaction was proposed. After introducing the BDC linker with the amine group -NH₂, the bandgap of MIL-125 was obviously reduced (Fu et al., 2012; Xu et al., 2015), and its optical absorption performance was improved. In addition, the adsorption capability toward CO₂ was also enhanced by the amino functionality. The HCOO⁻ yield increased to 3.83 μmol.

Even so, the NH₂-MIL-125 still has a low CO₂ reduction activity (Xu et al., 2015). To further improve the photocatalytic efficiency, graphene-like two-dimensional materials have often been incorporated into many photocatalysts via covalent or non-covalent interactions (Zhu et al., 2018). A microwave induction platform for the preparation of graphene oxide (GO)-enhanced MOF photocatalysts with highly efficient optical and electronic properties resulted in good photocatalytic oxidation performance and stability for nitric oxide and acetaldehyde (Li et al., 2018b). A strong photocatalytic hydrogen production activity up to ~9.1-fold that of the pure MOF can be achieved by MOF@rGO because the strong π-π interactions between the MOF and rGO can

effectively accelerate the electron-hole pair separation (Karthik et al., 2018).

Herein, a NH₂-MIL-125(Ti) and reduced graphene oxide (rGO) composite was synthesized *in situ* by a facile “one-pot” method as an efficient photocatalyst for CO₂ reduction. The bare MIL-125(Ti) was also prepared to compare with NH₂-MIL-125(Ti) in order to highlight the advantage of -NH₂ based on its superior optical performance. rGO with a two-dimensional structure was expected to be a superior charge transfer medium due to its fast light transmission, outstanding conductivity and high carrier mobility (Bao and Chen, 2018). Moreover, rGO was also supposed to play a part in the structural adjustment of NH₂-MIL-125(Ti). Therefore, the objective catalyst was compared to pure MIL-125(Ti) and NH₂-MIL-125(Ti) to ascertain the synergistic effect of the -NH₂-containing linker and incorporated rGO. The photocatalytic reaction here was conducted in a catalyst-methanol slurry system at normal atmospheric pressure and temperature. MeCN, TEOA and other toxic organic solvents were avoided for use as hole scavengers. Instead, hypotoxic methanol was chosen as the reducing agent due to its high CO₂ absorption capacity.

EXPERIMENTAL

Synthesis

Pure MIL-125(Ti) was prepared through a solvothermal process referenced in the literature (Yang et al., 2017; Rahmani et al., 2018; Wang et al., 2018c). Typically, titanium isopropoxide (1.5 mmol) and H₂BDC (6 mmol) were dissolved in a mixed solvent of DMF and CH₃OH (18 mL/2 mL) under magnetic stirring for 0.5 h. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 150°C for 72 h. After being filtered, the white solid product was washed thrice with DMF and CH₃OH, respectively. During the washing process, the suspension was subjected to natural precipitation and removal of the supernatant. Finally, the MIL-125(Ti) powder was activated under vacuum drying at 80°C for 10 h.

Amino-substituted titanium MOF NH₂-MIL-125(Ti) was also prepared by a similar procedure except that H₂BDC was replaced by H₂BDC-NH₂. Finally, a yellow solid powder was obtained.

The NH₂-MIL-125(Ti) and rGO composite was synthesized according to a similar solvothermal process. First, a certain amount of GO powder was dispersed into 10 mL DMF by ultrasonication for 1 h. The amount of GO added was 5 wt. % of the parent MOF. In the meantime, titanium isopropoxide (1.5 mmol) and H₂BDC (6 mmol) were dissolved in a mixed solvent of DMF and CH₃OH (18 mL/2 mL). Then, the above two were mixed together, stirred constantly for 1 h, and subjected to a solvothermal process at 150°C for 72 h. Usually, this solvothermal condition reduces GO to rGO (Yang et al., 2016a). The following procedures were the same as those for the above two pristine MOFs. The obtained gray powder was labeled as rGO@NH₂-MIL-125.

Characterization

The structures of all three obtained samples were measured by X-ray diffraction (XRD) (XD-3, Purkinjie), scanning electron

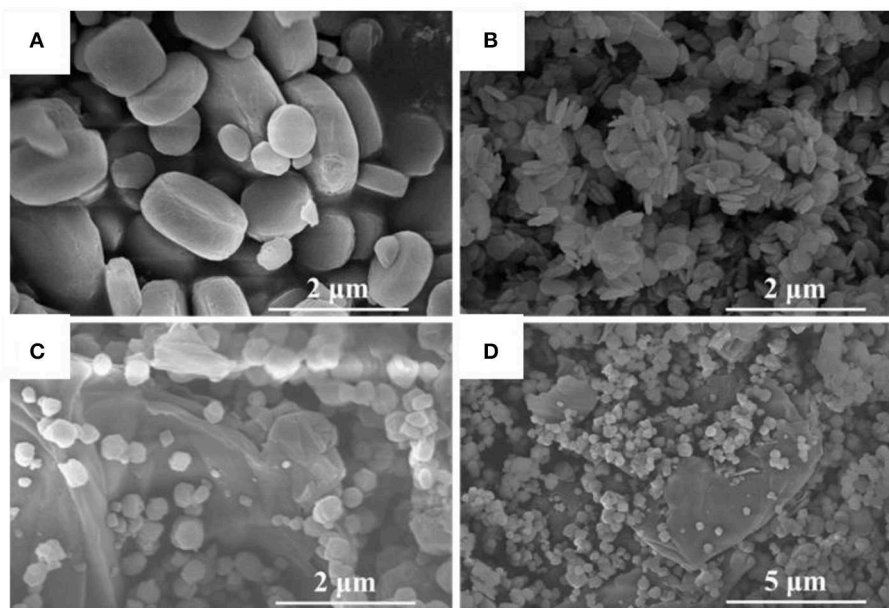


FIGURE 2 | SEM images of MIL-125 (A), NH₂-MIL-125 (B), and rGO@NH₂-MIL-125 (C,D).

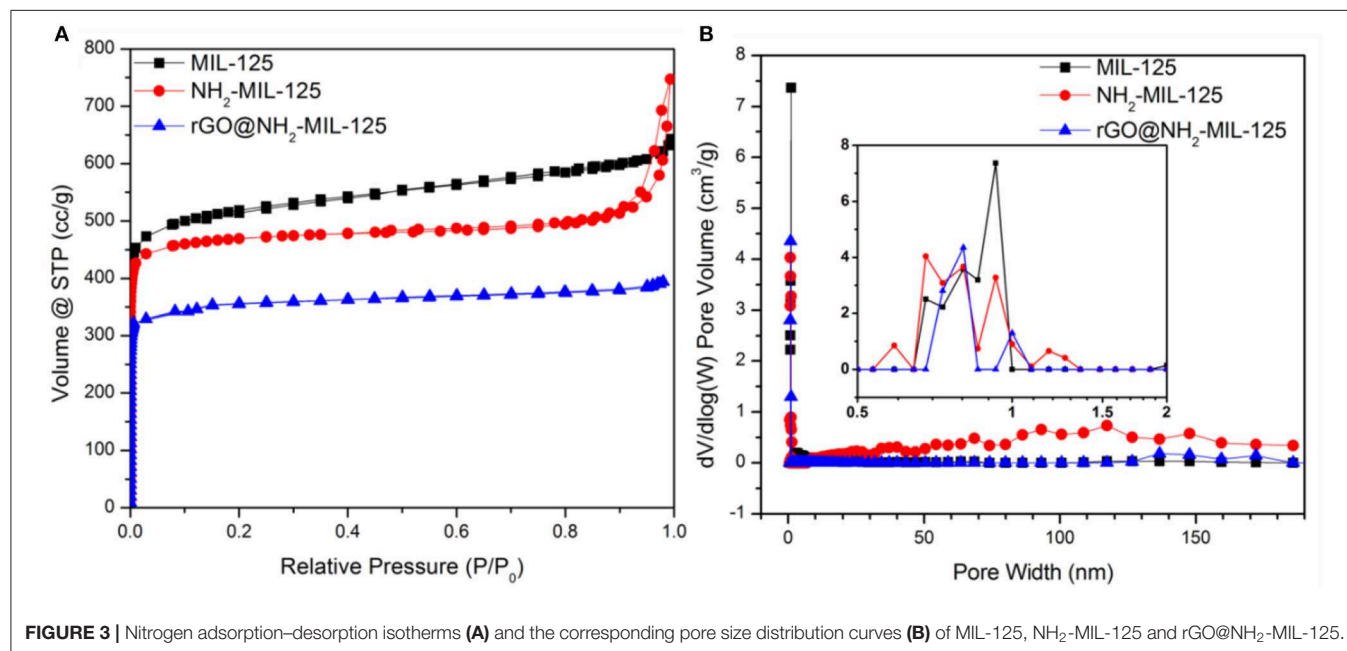


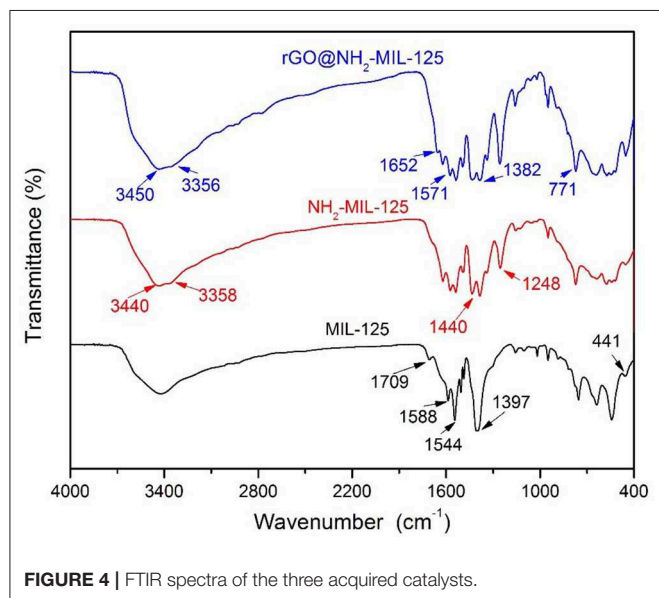
FIGURE 3 | Nitrogen adsorption-desorption isotherms (A) and the corresponding pore size distribution curves (B) of MIL-125, NH₂-MIL-125 and rGO@NH₂-MIL-125.

display Brunauer-Emmett-Telle (BET) surface areas of 1,669, 1,490, and 1,048 m²·g⁻¹, respectively. A higher surface area can provide more active sites for photocatalytic reactions. rGO@NH₂-MIL-125 possesses a smaller surface area and micropore volume than NH₂-MIL-125. Here, the intended content of GO added in the composite was 5 wt.%. However, the surface area of the rGO@NH₂-MIL-125 composite obtained was much less than the value on a prorata calculation. Therefore, the introduction of rGO affected the structure

of NH₂-MIL-125 particle agglomerates and decreased their surface area and pore volume. As seen from the pore size distribution curves, more mesopores exist in NH₂-MIL-125 based on the hysteresis loop observed in its N₂ adsorption-desorption isotherm. This difference may be caused by its aggregated clusters, and thus, NH₂-MIL-125 exhibits a larger total pore volume than MIL-125 and a similar micropore ratio. When rGO is incorporated into the reaction precursor, the obtained rGO@NH₂-MIL-125 exhibits a lower mesopore

TABLE 1 | Specific surface areas and pore structure parameters of the three as-prepared samples.

Samples	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$V_t/\text{cm}^3\cdot\text{g}^{-1}$	$V_{\text{micro}}/\text{cm}^3\cdot\text{g}^{-1}$	V_{micro}/V_t
MIL-125	1,669	0.99	0.62	63%
NH ₂ -MIL-125	1,490	1.15	0.64	56%
rGO@NH ₂ -MIL-125	1,048	0.71	0.55	77%

**FIGURE 4** | FTIR spectra of the three acquired catalysts.

volume and a more centralized pore width distribution, which is in agreement with its higher dispersibility relative to those of NH₂-MIL-125.

Chemical Composition

Figure 4 shows the comparison of the FTIR spectra of the pure MOFs MIL-125 and NH₂-MIL-125 and the composite rGO@NH₂-MIL-125. In the FTIR spectrum of MIL-125, the large broad adsorption band in the range of 3,200~3,700 cm⁻¹ is attributed to free solvent molecules in the framework pores (Yang et al., 2017). The strong bands at 1,397~1,709 cm⁻¹ are assigned to the vibrations of carboxylate groups, which belong to the linkers in the framework of MIL-125 (Martis et al., 2013; Wang et al., 2015; Yang et al., 2017, 2018). The characteristic absorption of benzene rings is observed in the range of 800~1,200 cm⁻¹, and the O-Ti-O vibrations are located in the range of 400~800 cm⁻¹ (Yang et al., 2017, 2018). NH₂-MIL-125 possesses three similar main absorption regions as MIL-125 except the characteristic stretching vibrations of the hydroxyl at 3,440 cm⁻¹ and the amino at 3,358 cm⁻¹ (Martis et al., 2013; Wang et al., 2015; Li et al., 2018b). In addition, the strong band at 1,248 cm⁻¹ is assigned to the stretching vibrations of C-N from the aromatic amine (Hadži and Škrbljak, 1957). rGO@NH₂-MIL-125 shows almost the same adsorption bands as NH₂-MIL-125. The absence of GO-related stretching bands for oxygen-containing functional groups confirms the effective reduction

of GO into rGO under the solvothermal reaction process. In addition, a new absorption band originating from the graphene skeletal vibration appears at 1,652 cm⁻¹, which is shifted from its common band position of 1,630 cm⁻¹ (Al Nafey et al., 2017; Zhao et al., 2017). This shift also hints at the interactions between rGO and MOF components in the rGO@NH₂-MIL-125 composite.

Optical Properties

The optical absorption characteristics of pure MIL-125, NH₂-MIL-125 and the composite rGO@NH₂-MIL-125 were investigated by UV-vis DRS in **Figure 5A**. For MIL-125, its absorption peaks are in the UV-light range, while the pure NH₂-MIL-125 and the composite rGO@NH₂-MIL-125 absorb light from the UV to visible-light range, which can improve the utilization of solar energy and produce more electron-hole pairs. For MIL-125, the O to Ti ligand-to-metal charge transfer in TiO₅(OH) inorganic clusters was confirmed by Sun and Li (2017) and Kim et al. (2013), and H₂BDC-NH₂ or rGO apparently influences the charge transfer phenomena in these TiO₅(OH) clusters in NH₂-MIL-125 or rGO@NH₂-MIL-125. Moreover, rGO@NH₂-MIL-125 possesses a higher absorption intensity than NH₂-MIL-125 at wavelengths >500 and 339~411 nm, indicating that the addition of rGO may positively affect the optical properties. In **Figure 5B**, the bandgap values can be determined from the plots of (Ahv)² vs. the photon energy (hv) by extrapolating the maximum slope to the x axis (Li et al., 2018b; Wu et al., 2018). For semiconducting MOFs, the bandgap is defined as the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) according to the molecular orbital method (Maina et al., 2017; Li et al., 2018a). Thus, the HOMO-LUMO gap of MIL-125 is 3.75 eV and that for NH₂-MIL-125 is 2.69 eV, which is very close to that of the composite rGO@NH₂-MIL-125 (2.75 eV). Thus, the introduction of the amino into the BDC linker can clearly reduce the HOMO-LUMO gap value of MIL-125. The photocatalyst with a higher HOMO-LUMO gap requires light with higher energy to generate photoinduced electrons and holes. Obviously, amino groups introduced into the linkers of MIL-125 are favorable for extending the optical adsorption properties and decreasing the photodriving force.

The trapping and lifetime of photogenerated charges has a great effect on the photocatalytic activity of a semiconductor photocatalyst (Liu G., et al., 2018; Liu H., et al., 2018). The PL spectra of the three catalysts are shown in **Figure 6** since PL is usually used for evaluating the recombination of photoinduced charge carriers. The pristine MIL-125 displays a strong peak at ~525 nm. However, the PL intensities of pure NH₂-MIL-125 and the composite rGO@NH₂-MIL-125 were significantly weakened. At the optimum wavelength of 525 nm, they are very close. However, in the higher wavelength scope, the intensity of rGO@NH₂-MIL-125 is even lower. Generally, the low PL intensity can result from a low recombination rate of photogenerated electron-hole pairs (Huang et al., 2018), suggesting the longer service life of the electron hole. Thus, both the amino-functionalized linker and the rGO incorporation

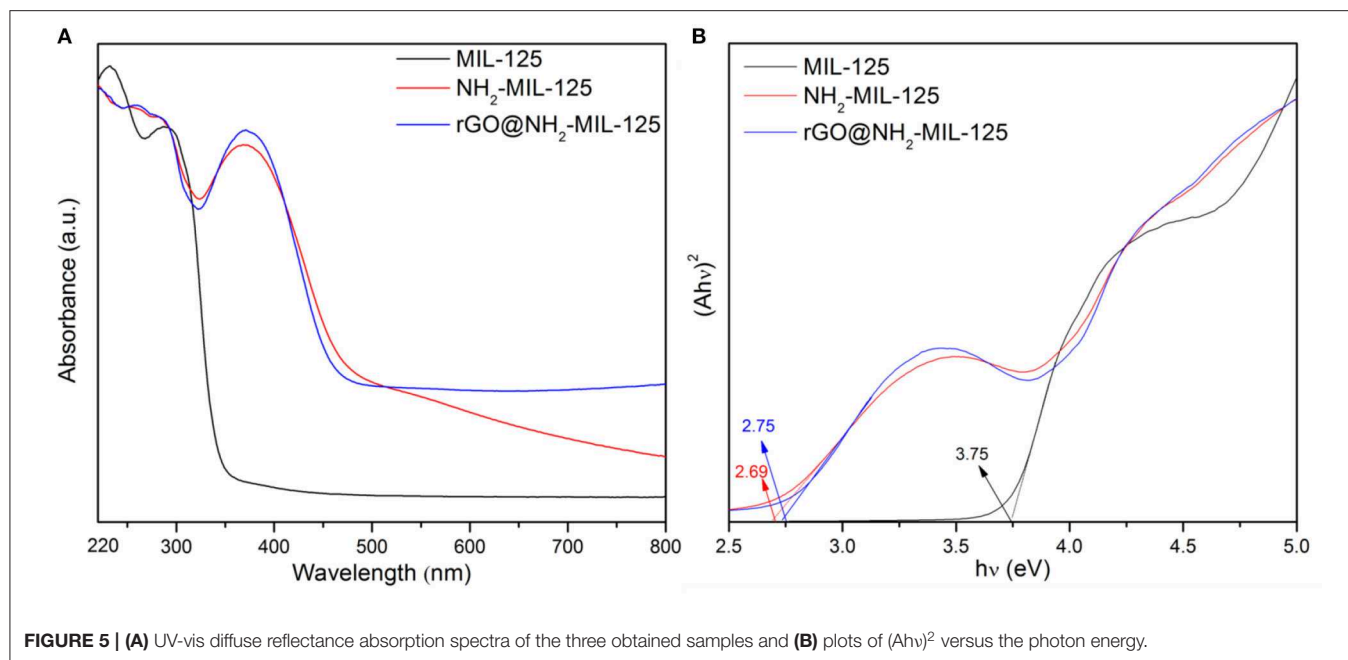


FIGURE 5 | (A) UV-vis diffuse reflectance absorption spectra of the three obtained samples and (B) plots of $(Ah\nu)^2$ versus the photon energy.

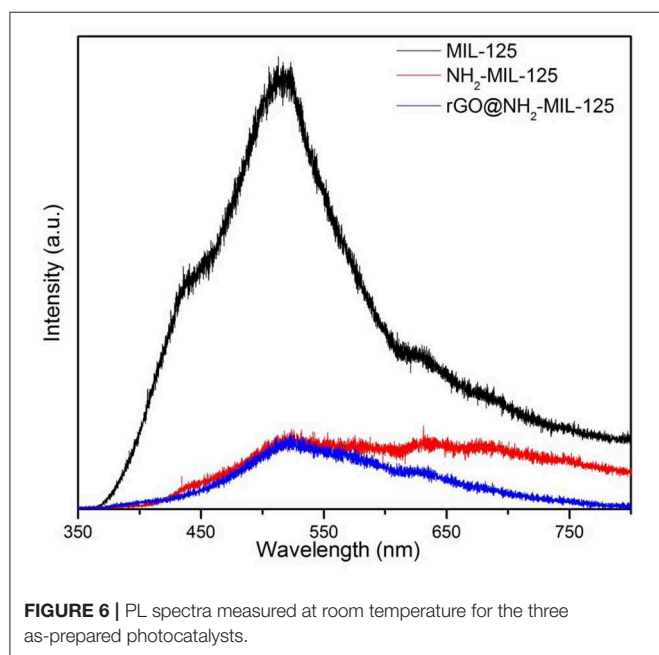


FIGURE 6 | PL spectra measured at room temperature for the three as-prepared photocatalysts.

are favorable for the mobility of photoexcited electrons and prohibiting photoinduced charge carrier recombination.

Photoelectrochemical measurements were performed to further study the charge separation and transfer efficiency of all catalysts. In **Figure 7A**, the three as-prepared samples display basically reproducible photocurrent responses during intermittent visible-light irradiation with the same time intervals. Clearly, the photocurrent densities decreased following the sequence of rGO@NH₂-MIL-125, NH₂-MIL-125, and MIL-125. A high photocurrent density is attributed to a high separation

efficiency of photogenerated electron-hole pairs (Wan et al., 2017a,b). Thus, both amino groups containing linkers and rGO benefit the efficient separation of photoinduced e⁻ and h⁺ for further improvement of enhancing the photocatalytic activity of MIL-125. The electrochemical impedance spectroscopy (EIS) test is another effective way to analyse the charge transfer properties. In theory, a smaller arc radius in the EIS Nyquist plot indicates a lower charge transfer resistance and represents a higher migration and transfer efficiency of photoexcited electron-hole pairs (Wan et al., 2017b; Wang et al., 2018d). In **Figure 7B**, the introduction of rGO and amino groups in MIL-125 causes a significant decrease in the arc radius, implying the lowest charge transfer resistance on the surface of the electrode with rGO@NH₂-MIL-125, which is consistent with the photocurrent results.

Photocatalytic CO₂ Reduction Performance

Figure 8A shows the photocatalytic activity of MIL-125, NH₂-MIL-125 and rGO@NH₂-MIL-125. These three materials were used to reduce CO₂ in CH₃OH after 4 h of light irradiation, and the predominant reaction product was MF. Since the light source was UV-light, the photon energy was enough to excite all the three photocatalysts. For the fresh samples, the data in the figure show that NH₂-MIL-125 has a slightly higher MF yield than MIL-125, although the former possesses a lower BET surface area. This difference might be related to the special structure and functional groups of NH₂-MIL-125. Excluding the surface area, the MF formation rate in units of μmol·m⁻²·h⁻¹ is shown in **Figure 8B**. This result for NH₂-MIL-125 is superior to that of MIL-125, which is attributed to its more effective separation of photoinduced charge carriers. Among these three samples, rGO@NH₂-MIL-125 exhibits the highest yield of MF, which is

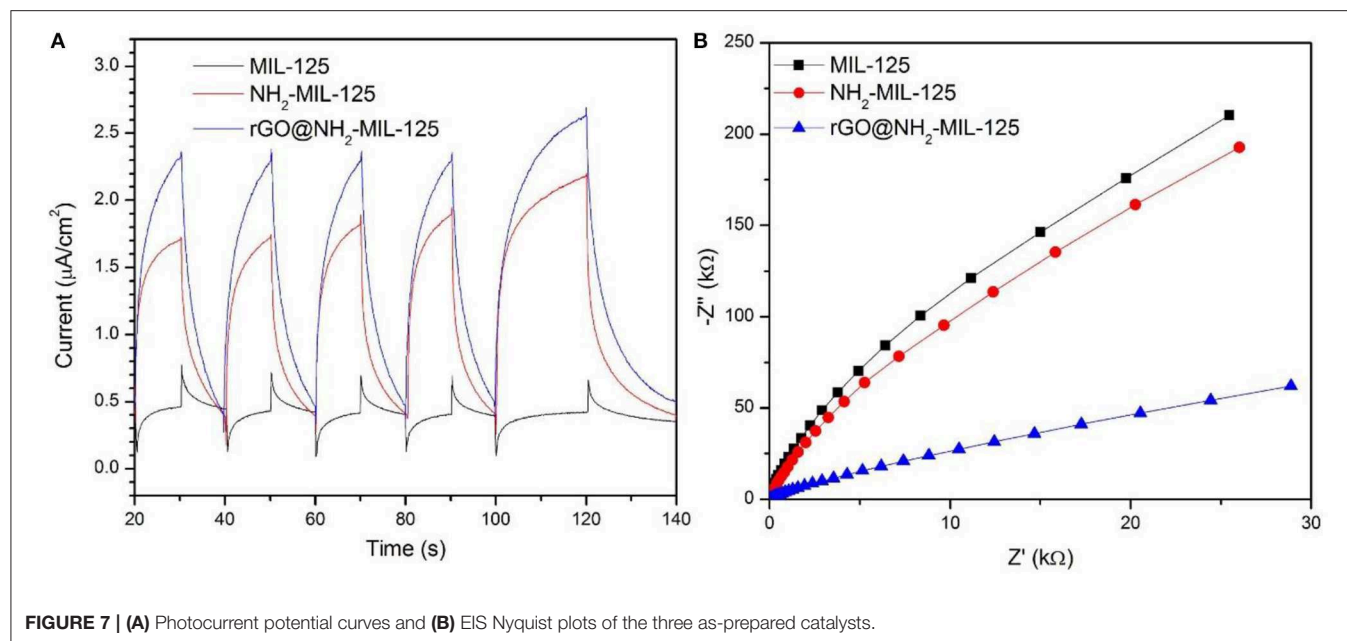


FIGURE 7 | (A) Photocurrent potential curves and (B) EIS Nyquist plots of the three as-prepared catalysts.

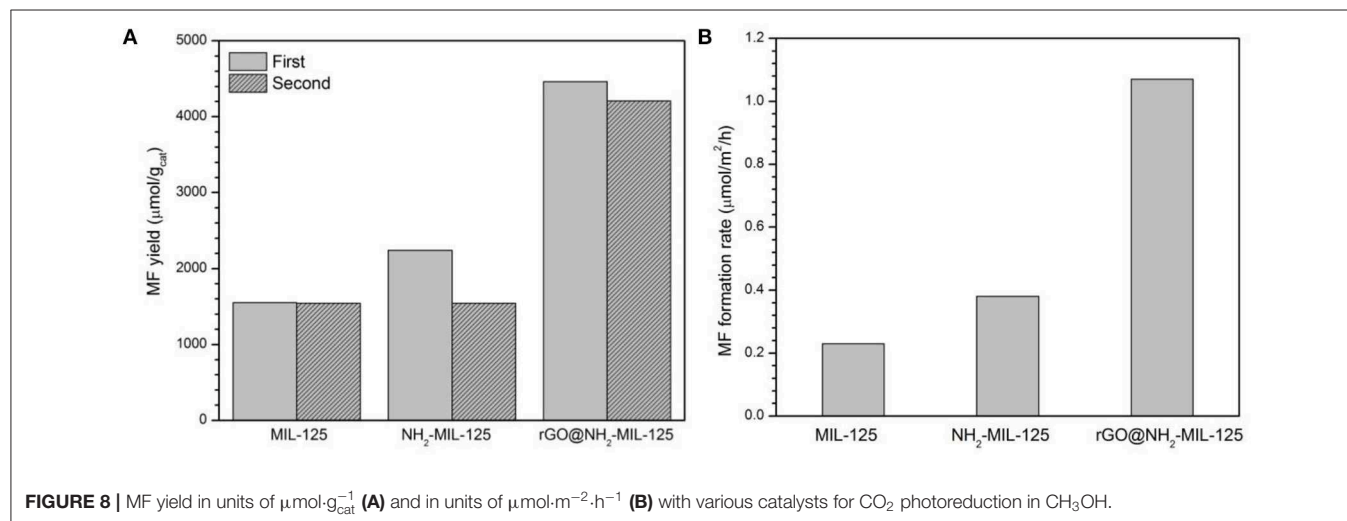
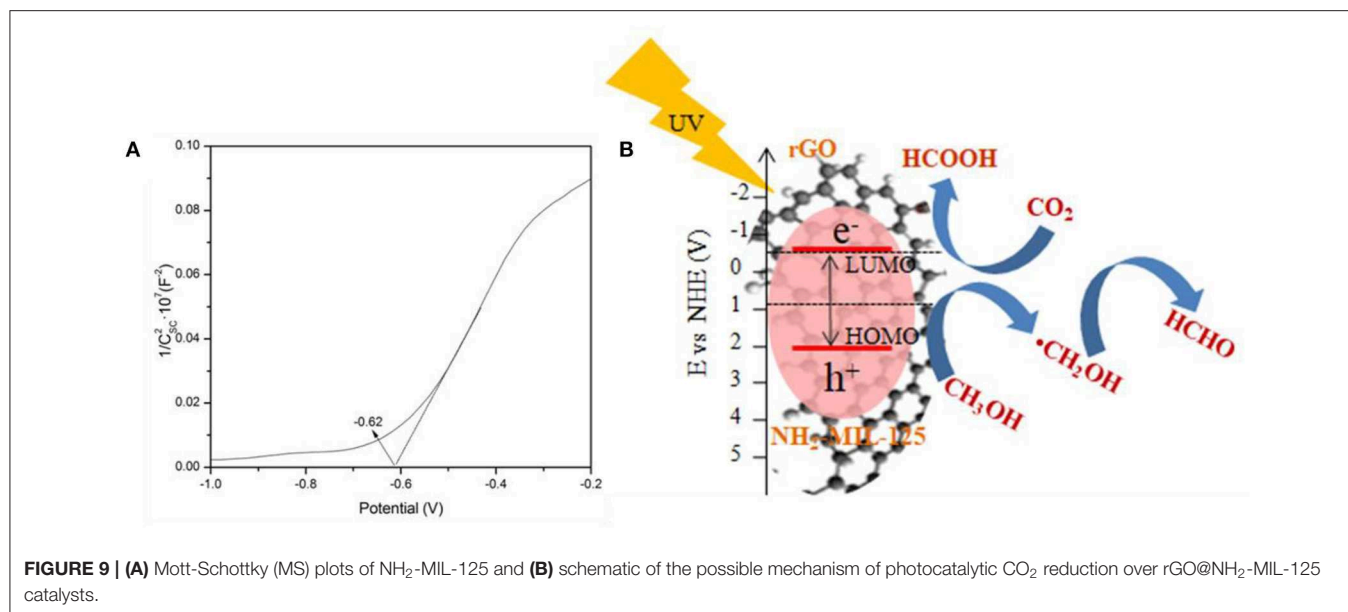


FIGURE 8 | MF yield in units of $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$ (A) and in units of $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (B) with various catalysts for CO₂ photoreduction in CH₃OH.

1,116 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and more than twice that of pure MIL-125. This is also more than that of metal sulfides (Chen et al., 2013a,b, 2015). In addition, the honeycomb lattice of rGO allows electrons to pass rapidly. It has good electron conductivity and results in the superior catalytic performance of rGO@NH₂-MIL-125. Thus, the high photoactivity of rGO@NH₂-MIL-125 can be ascribed to the effective spatial separation and transfer of photoinduced carriers, largely due to the synergistic effect of amino functionality and rGO incorporation.

The catalysts were recovered from the photocatalytic suspension system by centrifugation after each use. In Figure 8A, the repeatability of the NH₂-MIL-125 series sample is worse than that of MIL-125, which indicates the better stability of MIL-125. According to the XRD patterns of fresh and used samples after two cycles (Figure S2), there is no drastic change

on their crystal structure. Only the intensities of XRD patterns of used catalysts are decreased, which can be explained by some adsorbed species in them (Sadeghi et al., 2018). The FTIR spectra of the used samples (Figure S3) show some new bands at 2,800~2,900 cm^{-1} and 3,500~3,600 cm^{-1} from CH₃OH (Forester and Howe, 1987), indicating that the adsorbed species was methanol in the recycled catalysts. To further investigate the recyclability of rGO@NH₂-MIL-125 with the best photocatalysis activity, four times cycling tests of photocatalytic CO₂ reduction over it were conducted. As shown in Figure S4, the yields of MF are still above 85% after four cycles, which indicates acceptable recyclability of GO@NH₂-MIL-125 for photocatalytic CO₂ reduction. In the future, the stability of the photocatalysts in cyclic runs is expected to improve by optimizing the recycling operations.



To clarify the possible mechanism for the photocatalytic CO₂ reduction in CH₃OH solution over rGO@NH₂-MIL-125 catalysts under UV-light irradiation, the band structure of NH₂-MIL-125 was investigated by Mott-Schottky measurements, and the Mott-Schottky plot is shown in **Figure 9A**. The positive slope of the plot indicates that NH₂-MIL-125 is an n-type semiconductor (Yang et al., 2016a). If NH₂-MIL-125 is set as a conventional semiconductor, the X-axis intercept of -0.62 of the linear region can be considered its flat band potential (V_{fb}) with the unit V vs. Ag/AgCl. According to the equation (Ao et al., 2018; Cai et al., 2018; Wang et al., 2018d), E (NHE, normal hydrogen electrode) = $E(\text{Ag}/\text{AgCl}) + 0.1976$ V, the converted potential NHE is obtained. Since V_{fb} is generally 0.2 V more positive than the conduction band (CB) potential (E_{CB}) for an n-type semiconductor (Chen et al., 2013a; Wang et al., 2018d), the calculated E_{CB} is ~ -0.62 V vs. NHE. Based on the corresponding LUMO potential of NH₂-MIL-125 (-0.62 V) (Zhao et al., 2019) and the bandgap (HOMO-LUMO gap width) in **Figure 5A**, the position of the HOMO energy level is further estimated to be 2.07 V vs. NHE. Under UV-light irradiation, NH₂-MIL-125 can absorb photon energy and then be excited to generate electron-hole pairs. The electrons in the LUMO of NH₂-MIL-125 transfer to the rGO surface due to its excellent electron mobility (Li et al., 2018c; Zhu et al., 2018), while the holes can remain on the HOMO of NH₂-MIL-125 since the recombination of photogenerated charge carriers is greatly inhibited. As reported by Wan et al. (2017a), rGO itself doesn't contribute to the generation of electrons and holes under light irradiation. It only serves as an electron conductor medium. Thus, the introduction of rGO offers a greater range of carrier motion, which can efficiently suppress the recombination of photoinduced electrons and holes as well as increase the ability of electronic transmission. A possible mechanism is proposed, as displayed in **Figure 9B**, according to the above HOMO-LUMO structure. The HOMO of NH₂-MIL-125 is more positive than

the reported $E_0(\text{CH}_3\text{OH}/\text{CH}_2\text{OH})$ (0.927 V) (Qin et al., 2011; Yang et al., 2016b; Chen et al., 2017; Ao et al., 2018), so the photoinduced holes can oxidize CH₃OH into HCHO with H⁺ formation. The LUMO of NH₂-MIL-125 is negative than $E_0(\text{CO}_2/\text{HCOOH})$ (-0.61 V) (Qin et al., 2011; Yang et al., 2016b; Chen et al., 2017; Ao et al., 2018) and can reduce CO₂ into HCOOH in the presence of H⁺. Finally, MF can be produced not only via the esterification of HCOOH and CH₃OH but also by the dimerization of HCHO based on the Tishchenko reaction (Qin et al., 2011; Yang et al., 2016b; Chen et al., 2017).

CONCLUSIONS

The composite rGO@NH₂-MIL-125 was fabricated *in situ* through a "one-pot" solvothermal process. The agglomerated state of NH₂-MIL-125(Ti) was improved by introducing rGO. Its photocatalytic activity was evaluated by the photocatalytic CO₂ reduction in CH₃OH solution and compared with those of the other two prepared samples MIL-125 and NH₂-MIL-125. The results showed that MF was the predominant reaction product, and rGO@NH₂-MIL-125 exhibited the highest yield of 1,116 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is two times more than that of pure MIL-125. The effective separation of photogenerated electrons and holes largely due to the synergistic effect of amino functionality and rGO incorporation contributed to the high photoactivity of rGO@NH₂-MIL-125. It also displayed acceptable repeatability in cyclic runs for CO₂ photocatalytic reduction. However, its repeatability without achieving the largest value indicates that optimization of the recovery processes in future research can further improve the stability of the photocatalysts in cyclic runs.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

YZ did the experiment, analyzed the data and drafted the article. WC collected data and analyzed them. JC and YM assisted the work of YZ and WC. YB designed the work.

FUNDING

This research was supported by the National Natural Science Foundation of China (51802160 and 51808296), the Natural Science Foundation of Jiangsu Province (BK20150892 and

BK20170938), the Natural Science Foundation of Jiangsu Higher Education Institution of China (15KJB610012), and the 63rd Chinese Postdoctoral Science Foundation (2018M630487). YZ and WC appreciate the Start-up Funds for Introducing Talent of NUIST (S8113082001 and 2243141601034).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2019.00789/full#supplementary-material>

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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