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Abstract
© 2020 Hydrogen Energy Publications LLC Developing photocatalysts with superior efficiency and selectivity is an important issue for photocatalytic converting CO2. Hierarchically heterostructured one-dimensional nanomaterials represent a kind of promising catalysts for photocatalytic CO2 reduction on account of the high surface area and synthetic effect between different components. Herein, we synthesized UIO-66-NH2/carbon nanotubes (CNTs) heterostructures via a hydrothermal method, and investigated their photocatalytic performance. The element mapping, X-ray diffraction, and X-ray photoelectron spectroscopy collectively confirmed that the UIO-66-NH2 was successfully loaded on the surface of the CNTs. The specific surface area of the UIO-66-NH2/CNTs is 1.5 times higher than that of UIO-66-NH2. The photocurrent and electrochemical impedance spectroscopy measurements showed that the CNTs could enhance the electron mobility and reduce the recombination of photogenerated electron-hole pairs, which was also confirmed by the Photoluminescence spectroscopy (PL). The CNTs can improve the conductivity of composites and the dispersion of UIO-66-NH2, exposing more active sites, therefore the UIO-66-NH2 can increase the absorption of carbon dioxide and thus enhance the selectivity. The composites remarkably promoted the separation and transition of electrons and thus improved the photocatalytic efficiency of CO2 reduction. More importantly, it was found that the as-prepared composites suppress the hydrogen generation reaction during the CO2 reduction process.

Keywords
enhanced, activity, selectivity, over, photocatalytic, co2, fabrication, reduction, heterostructured, uio-66-nh2, /cnts

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**Keywords:** Carbon nanotubes; Photocatalytic activity; selectivity; UIO-66-NH₂; CO₂ reduction, HCOOH.

1. **Introduction**

The UN has been raising the alarm that the planet is getting hotter than ever before and is more prone to natural disasters such as flooding, hurricanes and tsunami as the amount of CO₂ in the earth’s atmosphere grew at a record rate to a level not seen for millions of years [1, 2]. Therefore, how to effectively reduce CO₂ level inevitably becomes an important issue nowadays[3].

Photocatalysis is an alternative technology that has great potential in various fields, because it is environmentally friendly and can directly make use of sunlight [4]. Photocatalysis has proven to be an ideal strategy to reduce CO₂ by using sunlight and converted CO₂ into hydrocarbons (such as HCOOH) that can serve as raw materials for the chemical industry [5-7]. Notably, HCOOH is a photocatalytic product derived from CO₂ reduction, which can be used as industrial raw materials and hydrogen storage materials [8-10]. However, the photocatalytic reduction efficiency of CO₂
and exclusive selectivity toward HCOOH are faced with enormous challenges. Most photocatalysts have weak adsorptive capacity of CO₂ and insufficient surface catalytic sites for photoreduction reactions. Appropriate design of efficient active and selective photocatalyst is vital to the photocatalysis because some byproduct caused by the inadequate and non-selective reaction process is a key challenge[11]. The interfacial structure performs a vital role for photogenerated charge transfer and molecular activation. In this case, the reactants and intermediates can be easily transformed to the aiming products with the help of electron-rich circumstance at the interface of composites, thus leading to the superior photocatalytic performance [12]. Developing an efficient photocatalyst is crucial to improve the photocatalytic efficiency of CO₂ reduction and selectivity toward main products.

Metal–organic frameworks (MOFs) that connected by metallic ions and organic ligands [13], have recently attracted numerous attention because of its unique physicochemical properties such as specific surface area, strong stability, high pore volume and excellent corrosion resistance [14]. MOFs have a wide range of applications such as gas adsorption, separation as well as catalysis [15]. In addition, MOFs have been regarded as excellent candidates for photocatalysis because they have unique porous structure which is favorable for mass transportation in photocatalytic reactions [16-18]. More importantly, it has the ability to absorb CO₂ thus improving the photocatalytic selectivity [19, 20]. Zr based MOFs have been widely applied in photocatalysis due to their high chemical stability and adequate redox potential of Zr (IV)/Zr (III) toward proton auxiliary CO₂ reduction [21, 22]. UIO-66 that based on a 3D structure of zirconium-oxo clusters is a typical Zr based MOFs [23]. However, it has weak ability to absorb CO₂ [24, 25]. Introducing the special functional groups into the skeleton of MOFs can solve this problem [26, 27].
UIO-66-NH₂ consisting of Zr⁴⁺ and 2-aminoterephthalic acid (ATA) ligands that are favorable for CO₂ adsorption [28]. Moreover, it has a large red shift in absorption induced by amino groups and thus can improve photocatalytic activity in reducing CO₂ under visible-light irradiation [29]. Despite the UIO-66-NH₂ can be used as photocatalysts directly, but the photocatalytic activity and selectivity are still unsatisfactory. In this regard, many researchers combine the UIO-66-NH₂ with other materials, such as metals, non-metals, carbon related materials and so on, aiming to improve the photocatalytic performance. Wu et al. investigated the photoreduction of CO₂ on CdS nanorods decorated on the surface of UIO-66-NH₂ via a facile room-temperature photodeposition method, which exhibit superior photocatalytic activity and stability. MOFs act as both supports and electronic providers that can trigger the reaction and thus improving their photocatalytic activity [30]. Jafarzadeh et al. reported that the UIO-66-NH₂ modified with CuO NPs can be used as a heterogeneous catalyst, the obtained catalyst is easily recycled and reused several times [31]. Xu et al. fabricated UIO-66-NH₂/NiO nanoparticles composites which showed the photocatalytic activity of H₂ evolution is 5 times higher than that of the UIO-66-NH₂ [32]. Liu et al. synthesized PbBiO₂Br/UIO-66-NH₂ composites through solvothermal method, the composites exhibited higher photocatalytic activity for RhB degradation due to the synergistic effect between the PbBiO₂Br and UIO-66-NH₂ [33]. However, it suffered from some limitations because of UIO-66-NH₂’s poor conductivity and photoinduced aggregation. Therefore, improving the conductivity and dispersibility of composite materials is one of the important strategies to improve the photocatalytic properties of materials.

Multi-walled CNTs (MWCNTs) have attracted attention because of their unique structures and interesting properties including excellent mechanical strength, outstanding chemical stability
and remarkable electrical conductivity [34-38]. The CNTs could induce the nanomaterials self-assembly onto the surface of CNTs to form hierarchical structures, which can enhance the photocatalytic performance [39]. CNTs is promising candidate supports for loading nanoparticles, especially in fabricating heterogeneous catalysts because of their high surface area, high electrical conductivity, and hollow geometric structure [39, 40]. More and more composites based on CNTs have been prepared and reported recently [9, 41, 42]. CNTs modified polyethyleneimine was found to be an effective photocatalyst to reduce CO$_2$ [43]. In this composite, CNTs act as conductive agents, which provide a conductor pathway for the high-speed flow of electrons, making it more reactive kinetics[44]. Yang et al. reported that the composites of SnO$_2$/CNTs possessed highly efficient photocatalytic activity. The enhanced photocatalytic performance is mainly ascribed to the CNTs could accelerate the transition of the electrons and the composites could suppress the recombination of electron-hole pair [45]. Arsalani et al. fabricated the photocatalysts of ZnO/CNTs which displayed superior photocatalytic degradation efficiency than the pure ZnO [46]. The enhancement of photocatalytic efficiency of composites is ascribed to the CNTs could facilitate the transition of electrons and retard the recombination of photogenerated electron-hole pairs.

Considering the above concerns, composites based on the UIO-66-NH$_2$ and CNTs may provide smooth transfer channels for photoinduced electrons (e$^-$), short migration distance along the directional migration, inhibit the recombination of photogenerated charge carriers and thus improve the photocatalytic activity. In addition, CNTs have a large surface area that could inhibit the aggregation of MOFs, increase CO$_2$ adsorption site, enhance the adsorption of CO$_2$ and thus improve the selectivity. To the best of our knowledge, the report regarding decorating the
UIO-66-NH₂ with CNTs yet to be investigated. In this work, hierarchically heterostructured UIO-66-NH₂/CNTs nanomaterials were prepared via the hydrothermal method, which exhibited high photocatalytic activity and selectivity under visible light than that of the UIO-66-NH₂. Based on the experiments and analyses, a possible reaction mechanism of UIO-66-NH₂/CNTs was also proposed.

2. Materials and methods

2.1 Pretreatment of carbon nanotubes

The CNTs were treated with acid solution. The specific steps are as follows: the 1 g CNTs were dispersed in the 40 mL mixed acid solution, wherein the volume ratio of concentrated nitric acid to concentrated sulfuric acid was 3:1 and heated it at 80°C for 2 hours under reflux condition in an oil bath. After that the sample was washed with deionized water and dried overnight in an oven at 80°C.

2.2 Preparation of photocatalysts

All the chemicals were analytical grade and used without further purification. The composite photocatalyst UIO-66-NH₂/CNTs was fabricated by hydrothermal method at 120 °C for 12 h in a Teflon autoclave. Before the experiment, CNTs (1 wt%-5 wt%) were highly dispersed in a 50 mL N, N-dimethylformamide (DMF) under ultrasonic for over 1h. After uniform dispersion, 90 mg of 2-amino-terephthalic acid and 120 mg of zirconium (IV) chloride were added to the above solution (first added the 2-amino-terephthalic acid, then added the zirconium (IV) chloride), with ultrasonication for another 20 min and stirring for 20 min until 2-amino-terephthalic acid and zirconium (IV) chloride was completely dissolved. The as-formed solution was then transferred into an 80 mL Telton-lined stainless-steel autoclave. The autoclave was sealed and heated in an
electric oven at 120 °C for 12 h. After cooling naturally, the obtained sample was centrifuged and washed with DMF, methanol, and ethanol several times in turn. The final product was dried under vacuum drying oven at 80 °C for 24 h. The as-obtained composite photocatalyst was named as UIO-66-NH₂/x wt% CNTs (x = 1, 2, 3, 4, 5). Meanwhile, composites were also prepared through mechanically mixing.

2.3 Characterization

Structures were characterized by XRD with an X’pert MPDPro (PANalytical Co) by using Cu Kα radiation at 40 kV and 40 mA, 2 theta varied from 5° to 80°. Field emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI SU6600 (Japan) instrument. Transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS) spectrums were analyzed through a JEOL JEM2100 (Japan). The Raman spectrometer was used in this study which has a wavelength of 535 nm for excitation wavelength, which is made by HORIBA JOBIN YVON company, the HR 800 micro laser. The Brunauer Emmett Teller (BET) specific surface areas (S_BET) of the samples was determined at liquid nitrogen temperature (-196 °C) using an ASAP 2020 instrument. UV-visible (UV-vis) diffused spectroscopy of the samples were recorded on a HITACHI UV4100 spectrometer operating between 200 nm to 800 nm wavelength, using BaSO₄ as the reflectance standard.

2.4 Photoelectrochemical (PEC) measurements

Photoelectrochemical measurements were carried out on a CHI660D (China) electrochemical workstation. A 500 W Xe lamp with a cutoff glass (λ> 400 nm) as the light source. The distance between the light and the Pyrex glass beaker was 12 cm. The working electrode (2cm x 1cm) was based on FTO glass, which were prepared with mixing photocatalyst(25 mg), polyethylene glycol
(20 mg) and ethanol(200 µl). Then the working electrode was annealed at 200 °C for 120 min in N2 atmosphere. In the PEC measurements, platinum sheets (99.99%) were served as a counter electrode, Ag/AgCl used as reference electrode and 0.5M Na2SO4 electrolyte solution was used.

2.5 Photocatalytic activity for the reduction of CO2

The photocatalytic reduction of CO2 was performed in a homemade glass reactor with 40 mL DMF (solvent of CO2), 5 mL triethanolamine (TEOA-sacrificial agent), 3 mL H2O (proton source). Before irradiation, the mixture gas (50% Ar and 50% CO2) was bubbled for 30 min into the solution until the concentration of CO2 reached saturation and the dissolved oxygen was removed completely. Irradiation (light source: 500 xenon lamp, λ > 400 nm).

After 4 h of illumination, 0.6 mL of sampled gas was analyzed via gas chromatograph (Agilent Technologies: 6890 N) with TCD detector to detected CO2. Carrier gas: Helium (99.999%). Columns: 5Å’ molecular sieve. The test conditions are: TCD temperature is 150 °C, the temperature of the hot wire is set to 200 °C, the inlet temperature is 100 °C. The amount of H2 evolution was also determined on this gas chromatograph using N2 as the carrier gas. The formic acid was detected by ion chromatography equipped with CD detector, RFC-30 on-line electrolytic leaching fluid generator, Dionex ionpac AS18 4*250mm chromatographic column. The selectivity of HCOOH was calculated via the formula:

\[
\% \text{ selectivity of HCOOH} = \frac{\text{HCOOH} (\mu\text{mol})}{\text{CO2 Reduction (\mu\text{mol})}} \times 100\%
\]

3. Results and discussion

3.1 The whole process of fabricating the photocatalysts

A facile approach for fabricating the composites of UIO-66-NH2/CNTs in this study. The composites were obtained through hydrothermal method, the formation mechanism of
nanocomposites is shown in Scheme 1. The nanostructures showed a large surface area and other superior properties which are essential to the enhancement of the photocatalytic performance.

![Scheme 1. The process of preparing composites of UIO-66-NH₂/CNTs.]

3.2 Structure characterization and Morphology analysis

The crystallinity of the CNTs, UIO-66-NH₂ and UIO-66-NH₂/2 wt% CNTs composites were evaluated by XRD. The XRD patterns of the as-prepared samples are shown in Fig. 1(a), the diffraction peaks of UIO-66-NH₂ were found at 2θ values of 7.36°(111), 8.48°(002), 12.04°(022), 17.08°(004), 22.25°(115), 25.68°(224) and 33.12°(137), well agreeing with that of previous reports, all the characteristic peaks are sharp and intensive which implied that the UIO-66-NH₂ had an excellent purity and crystallinity [15, 16, 27, 47]. As for the CNTs, the strong and wide diffraction peaks found at 2θ values of 26.24°(002) reflected the hexagonal graphite structure and the weak peak at 43.90°(100) associated with graphite, which is corresponded to the MWCNTs [48].

In the composites, all the diffraction peaks can be indexed to planes of crystalline phase of UIO-66-NH₂. There is no apparent characteristic peaks of CNTs in composites which due to its low content and shield with the peaks of UIO-66-NH₂. It shows the same tendency as other composites which are shown in Fig. S1(a). We also compared the nanocomposites obtained
through various synthesis routes. The XRD patterns of UIO-66-NH$_2$/2 wt% CNTs samples prepared with hydrothermal method and mechanical method are shown in Fig. S2(a), which illustrates the samples that fabricated through hydrothermal method had a higher purity and crystallinity than the samples prepared with the mechanical method. It is beneficial to enhance the photocatalytic performance. As shown in Fig. 1(b), the pure CNTs exhibited a typical in-phase vibration of the graphite lattice (G band) at 1575 cm$^{-1}$ and a disorder band owing to the graphite edges (D band) at approximately 1355 cm$^{-1}$ [49, 50]. The G band results from in-plane stretching motion of symmetric sp$^2$ C-C bonds and the D band appear because of disruption of symmetrical hexagonal graphitic lattice [51]. Upon loading UIO-66-NH$_2$ crystals, it was observed that both G and D bands of composites were broadened. These results showed that there has a strong interaction function between UIO-66-NH$_2$ and the CNTs during the synthesis process[52]. The similar phenomenon can be found in other samples(Fig.S1(b)). Fig. 1(c) shows the pure UIO-66-NH$_2$ particles, which present a cube structure with severe aggregation. Fig. 1(d) shows the diameter of CNTs is about 20-30 nm. In contrast, as shown in Fig. 1(e), after introducing the CNTs, UIO-66-NH$_2$ nanoparticles were uniformly grew on its surface. The uniform loading of UIO-66-NH$_2$ particles may strengthen the multiple reflections between crystals under visible light, which is more favorable to the conduction of electrons and beneficial to promote the photocatalysis reaction process. The SEM image of UIO-66-NH$_2$/2 wt% CNTs sample prepared with the mechanical method is shown in Fig. S2(b). It is obvious that the UIO-66-NH$_2$ and CNTs are just a physical mixture, scattering independently in the system and there is no synergistic effect between them.
Fig. 1. (a) The XRD patterns of CNTs, UIO-66-NH$_2$ and UIO-66-NH$_2$/2 wt% CNTs composites, (b) the Raman spectra of the CNTs, UIO-66-NH$_2$ and UIO-66-NH$_2$/2 wt% CNTs composites, the SEM images of (c) UIO-66-NH$_2$, (d) CNTs and (e) UIO-66-NH$_2$/CNTs.

To further analyses the structure of samples, the TEM and high-resolution TEM (HRTEM) measurements are carried out. Fig. 2(a) reveals that the UIO-66-NH$_2$ is nanosized particles and Fig. 2(b) shows the pure CNTs presenting a hollow tubular structure. Fig. 2(c) shows the TEM image of an individual CNTs densely deposited by UIO-66-NH$_2$ particles. The HRTEM image collected from the interface region in Fig. 2(f) indicates that there existed a strong interaction between UIO-66-NH$_2$ and CNTs. The pure CNTs is only consisted by C(red) element (Fig. 2 (d-e)). As shown in Fig. 2 (g-i), the element mapping image of UIO-66-NH$_2$/CNTs clearly shows the distribution of C(red) and Zr(green) elements in the composites. All of these elements are distributed uniformly in the composite samples, indicating that the good functionalized of CNTs with UIO-66-NH$_2$ under hydrothermal process and uniform distribution of UIO-66-NH$_2$ particles on the surface of CNTs.
Fig. 2. TEM images of UIO-66-NH$_2$(a), CNTs(b) and UIO-66-NH$_2$/CNTs(c), the images and mapping of CNTs(d-e), UIO-66-NH$_2$/CNTs((g-i), HRTEM images of UIO-66-NH$_2$/CNTs composites in (f).

XPS measurements have been carried out to ascertain the detail of the surface chemical state of the sample. The survey spectrum (Fig. 3(a)) indicates that the sample is composed of C, N, O, Zr. The C 1s spectrum is shown in Fig. 3(b), the composites show three peaks that located at 284.6, 285.4 and 289.0 eV, which are attributed to sp$^2$ C=C and sp$^2$ C–C bond of CNTs [53, 54], defect-containing sp$^2$-hybridized carbon, the C-NH$_2$ species and O=C-O of CNTs respectively [55, 56]. More interestingly, the C=C peak shows a attenuation in composites UIO-66-NH$_2$/CNTs, due to the interfacial charge transfer from UIO-66-NH$_2$ to CNTs and a strong interaction existed between the UIO-66-NH$_2$ and CNTs. The formed heterostructures generate interfacial electric fields and thus enhance the electron density of catalytically active sites.

The N 1s XPS spectrum (Fig. 3(c)) of the composite sample is located at 399.2 eV, while no difference has been observed compared with that of UIO-66-NH$_2$ [57], suggesting that the NH$_2$
groups on the organic linkers can be retained after loaded CNTs. The high-resolution XPS spectrum of the O1s orbital in the UIO-66-NH$_2$ can be fitted by two peaks at binding energies of around 531.5 and 531.0 eV (Fig. 3d), which are attributed to oxygen components on the carboxylate groups of the ATA linkers and the Zr-O bonds of UIO-66-NH$_2$, respectively [41, 47]. The O 1s of UIO-66-NH$_2$/CNTs are located at 531.5 eV and 530.0 eV. It shifts slightly compared to the UIO-66-NH$_2$ peaks which may due to the surface adsorption water had been replaced by the CNTs. The curves of Zr 3d region (Fig. 3e) can be deconvoluted into two peaks for Zr 3d$_{5/2}$ and Zr 3d$_{3/2}$ located at around 182.6 eV and 185.1 eV respectively, which indicates the existence of Zr$^{4+}$ [58].

**Fig. 3.** XPS survey spectra of CNTs, UIO-66-NH$_2$ and UIO-66-NH$_2$/CNTs(a), high resolution spectra of C 1s(b), N 1s(c), O 1s(d), Zr 3d(e) obtained from CNTs, UIO-66-NH$_2$ and UIO-66-NH$_2$/CNTs.

### 3.3 BET analysis
Fig. 4(a) and Fig. 4(b) shows the N\textsubscript{2} adsorption-desorption isotherms and the pore size distribution of the different samples. The materials show type IV isotherms suggested a mesoporous structure of composite materials. The sample of CNTs has the type H\textsubscript{3} hysteresis loop while the others have H\textsubscript{1} hysteresis loop, which is related to a compact structure of aggregated particles with uniform size and high connectivity between pores. The pore size distribution further confirmed that the samples had well-defined mesopores. The mesoporous structure could improve the adsorption capacity and photocatalysis performance because they provide high surface area, homogeneously porous structure and tunable framework [59-61].

The unique porous characteristics are favorable for transporting ions and electrons. Therefore, the photocatalytic reactions will be efficiently improved. The N\textsubscript{2} adsorption/desorption curves and pore size distribution of other samples are shown in Fig. S3(a) and Fig. S3(b).

Table 1 summarizes the specific surface area and pore size distribution of the samples. CNTs have a BET surface area of 82.10 m\textsuperscript{2}/g, while pure UIO-66-NH\textsubscript{2} exhibited a large surface area of 448.7 m\textsuperscript{2}/g. It is found that when the content of CNTs is 2 wt\%, the specific area of the composite is the highest, as well as the pore volume and average pore size. This inferred that the content of CNTs has an optimal value. The appropriate content of CNTs not only disperse UIO-66-NH\textsubscript{2}, but also increase the surface area, pore volume and average pore size of the composite materials. As increasing the surface area of composites, contact areas between active sites and target substrates are also increased thus causing superior photocatalytic performance. Besides, the studies showed that the increase of surface area could promote the acceptance of electrons and make the photocatalysts have a strong contact with active molecules. Thus the high surface area of composites would be conducive to supplying more reaction sites [62].
Fig. 4. N₂ adsorption/desorption curves(a) and pore size distribution(b) of the different samples.

Table 1

The surface area and pore structure for different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT (g)</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>0</td>
<td>82.10</td>
<td>0.5348</td>
<td>69.60</td>
</tr>
<tr>
<td>UIO-66-NH₂</td>
<td>0</td>
<td>448.7</td>
<td>0.7137</td>
<td>100.6</td>
</tr>
<tr>
<td>UIO-66-NH₂/1 wt% CNTs</td>
<td>0.01</td>
<td>523.5</td>
<td>0.5724</td>
<td>81.60</td>
</tr>
<tr>
<td>UIO-66-NH₂/2 wt% CNTs</td>
<td>0.02</td>
<td>642.5</td>
<td>0.6300</td>
<td>83.00</td>
</tr>
<tr>
<td>UIO-66-NH₂/3 wt% CNTs</td>
<td>0.03</td>
<td>444.1</td>
<td>0.6231</td>
<td>76.50</td>
</tr>
<tr>
<td>UIO-66-NH₂/4 wt% CNTs</td>
<td>0.04</td>
<td>398.9</td>
<td>0.5907</td>
<td>75.70</td>
</tr>
<tr>
<td>UIO-66-NH₂/5 wt% CNTs</td>
<td>0.05</td>
<td>331.5</td>
<td>0.5370</td>
<td>67.10</td>
</tr>
</tbody>
</table>

3.4 UV–vis spectra analysis

To provide further investigation, the optical properties of different samples are measured through the UV-vis spectra. As Fig. 5(a) shown, there is a slight blue shift in wavelength of absorption peak of composites. This phenomenon is attributed to the fact that UIO-66-NH₂ and CNTs are different two organic and inorganic phases. The composite samples possessed an
obviously enhanced absorption intensity in the visible light region compared to the sample of UIO-66-NH$_2$ which is due to presence of black CNTs. The pure UIO-66-NH$_2$ exhibited a response with a wavelength below 440 nm. The weak absorption of visible light possibly ascribed to the aggregation of UIO-66-NH$_2$ which is also demonstrated in SEM image mentioned above. The enhanced light harvesting of composites due to the good assembly of UIO-66-NH$_2$ particles along the surface of CNTs, thus raising the multiple light reflections in the materials. All of the samples show similar light absorbance attributed to their similar structure and based on the UIO-66-NH$_2$ (Fig. S4). Besides, the higher light absorption capacity of composites than UIO-66-NH$_2$ corresponding to the color change from greenish-yellow to grayish brown. Furthermore, it is due to the CNTs could effectively disperse UIO-66-NH$_2$ and enhanced its absorption strength of visible light [63].

The FTIR spectra of adsorbents presents three noticeable characteristic bonds, which locates at 1655 cm$^{-1}$, 1580 cm$^{-1}$ and 1400 cm$^{-1}$, respectively(see in Fig.5(b)). These three peaks are attributed to aromatic C=C stretching vibration, the vibration of carboxyl groups and C-H deformation vibration from -CH$_3$ and -CH$_2$[64]. Besides, the spectra of UIO-66-NH$_2$ also shows the typical peaks of N-H stretching at 1260 cm$^{-1}$ and 788 cm$^{-1}$, demonstrating the existence of -NH$_2$ group [65]. After combining the UIO-66-NH$_2$ and CNTs, the peak at 1655 cm$^{-1}$ has a noticeable change, portending the π-π interactions between them [66]. Comparing with the pure UIO-66-NH$_2$, the spectra of composites is relatively unchanged, while the strength of the peak decreased. There are some small changes in the composites, this is due to the introduction of functional groups that are brought with the surface of CNTs, moreover, carboxyl coordinated with metal ion altered the chemical circumstance of the ligand slightly [67].
3.5 Photocatalytic performance tests

The photocatalytic activities of various photocatalysts were evaluated under visible light illumination displayed in Fig. 6. In Fig. 6(a), it is evident that photocatalytic activity of CO₂ reduction increased firstly and then decreased while the generation of hydrogen shows the opposite trend. When the loading amount of CNTs is 2 wt%, the reduction of CO₂ reaches a maximum of 28.8 μmol while the H₂ generation shows a minimal amount of 2.0 μmol. The reduction of CO₂ and evolution of hydrogen are two electrons reaction process. They compete for the electrons in the photocatalytic system at the same time. The detailed data are shown in Table 2, all nanocomposites exhibit superior photocatalytic performance compared to the pure UIO-66-NH₂ which presents the synergistic effect of CNTs in these samples and the fact that CNTs improve the activity and selectivity of photocatalysts. With massive loading content of CNTs, the photocatalytic performance decrease, this is due to the fact that photons are further absorbed and scattered in the existence of CNTs. Besides, the excessive CNTs can play as a kind of recombination center instead of supplying an electron pathway.

Furthermore, we pursued selectivity of HCOOH changes. From Fig. 6(b), when the CNTs loading content changes from 0 to 2 wt%, the yield of HCOOH changes from 1.84 μmol to 18.2
μmol and the selectivity changes from 38.3% to 63.1%. When the CNTs loading content continues to increase from 2 wt% to 5 wt%, the yield of HCOOH has a gradual downward trend, while the selectivity also decreased. When the loading content of CNTs is 2 wt%, the yield of HCOOH and the selectivity reached a maximum value of 63.1%. The selectivity is almost 2 times higher than the pure UIO-66-NH₂. The improved selectivity is due to the absence of -NH₂, the physical adsorption sites and chemical reaction adsorption sites increased, the absorption reaction between CO₂ and -NH₂ enhanced the adsorption capacity of CO₂ significantly, therefore improve the selectivity of HCOOH. This has also been demonstrated by previous reports [68]. In addition, we obtained composite samples through mechanical mixing method and thus demonstrate the advantages of hydrothermal synthesis (Table S1).

As listed in Table S1, the UIO-66-NH₂/2 wt% CNTs sample fabricated through hydrothermal method exhibited higher HCOOH evolution amount (28.8 μmol), which is 2.1 times higher than the mechanical mixing sample (13.6 μmol). The selectivity of HCOOH is also nearly 2 times higher than the mechanical mixing sample. The hydrothermal process induced shaping UIO-66-NH₂ crystals on the surface of CNTs, increased its dispersibility and strengthened the contact between the UIO-66-NH₂ and CNTs. These merits supplied a short pathway for charge transfer and low charge transfer resistance during the photocatalysis process.

Most studies showed there exist two reaction pathways in the process of reducing CO₂, hydrogenation and deoxygenation of CO₂. On the basis of our experiments, we propose the photoreduction of CO₂ with water over UIO-66-NH₂/CNTs occurs via hydrogenation reactions, because the HCOOH is finally observed which consistent with previous reports [69]. The proposed reaction pathways are as following equations((1)-(6)), which is similar to the relevant
studies [70]. The represents absorbed species, hv indicates a photon under visible light. Under illumination, the UIO-66-NH$_2$ produced photogenerated electron(e$^-$)-hole (h$^+$) pairs. The holes will react with water molecules, forming *OH and H* intermediates. Then the H$^+$ react with the electrons and generate the H$_2$. The generation of HCOOH is based on a fast hydrogenation process of CO$_2$ on the interface of UIO-66-NH$_2$ and CNTs. With the H* intermediates, the HCOOH forms mainly because it is two electrons reaction process, easily than generates the other products, such as CH$_4$, CH$_3$OH. Besides, in this photocatalytic reaction system, the TEOA was used as sacrifice agent. According to previous reports, TEOA can also facilitate the photocatalytic CO$_2$ reduction because of its more basic nature, the presence of TEOA supports the hydrogenation of CO$_2$ to formate [71]. Effective hydrogen transfer catalysts should also be effective in the reduction of CO$_2$ and therefore inhibit the production of hydrogen.

As shown in Fig. 6(c), after six cycles of CO$_2$ photoreduction under visible light irradiation, the reduction of CO$_2$ was well maintained. This indicated the activity of composites kept relatively stable. These results indicated that the photocatalyst prepared with hydrothermal method has higher chemical stability to reduce CO$_2$ at ambiance conditions. The morphology of photocatalyst and valence state of the elements after the reusability test show no clearly change, as shown in Fig S5, the numerous UIO-66-NH$_2$ particles are deposited on the surface of CNTs, this demonstrates the stability of composites. As for the XPS, The survey spectrum (Fig. S6(a)) shows that the sample after the reusability test is composed of C, N, O, Zr. The C 1s spectrum is shown in Fig. S6(b), there are three peaks(284.6, 285.4 and 289.0 eV), The O 1s(Fig. S6(c)) are located at 531.5 eV and 530.0 eV. The curves of Zr 3d region (Fig. S6(d)) can be deconvoluted into two peaks, Zr 3d$_{5/2}$ (182.6 eV) and Zr 3d$_{3/2}$(185.1 eV), which indicates the existence of Zr$^{4+}$, all these results are
accordance with the sample before reusability test.

\[
\text{UIO-66-NH}_2 + \text{hv} \rightarrow \text{e}^- (\text{CB}) + \text{h}^+ (\text{VB}) \quad (1)
\]

\[
\text{H}_2\text{O}^+ + \text{h}^+ \rightarrow \text{OH}^- + \text{H}^+
\]

\[
\text{H}^+ + \text{e}^- \rightarrow \text{H}_2
\]

\[
\text{CO}_2 (g) \rightarrow \text{CO}_2^-
\]

\[
\text{CO}_2^+ + \text{H}^+ \rightarrow \text{HCOO}^-
\]

\[
\text{HCOO}^+ + \text{H}^+ \rightarrow \text{HCOOH}
\]

**Fig. 6.** The evolution of H\(_2\) and the conversion of CO\(_2\) (a), the evolution of formic acid and selectivity of HCOOH (b) of various photocatalysts under visible-light (\(\lambda > 420\) nm) irradiation.

Photocatalytic reduction of CO\(_2\) over sample UIO-66-NH\(_2\)/2 wt% CNTs after 6 cycles (c).

**Table 2**

The conversion of CO\(_2\), the evolution of various products, and the selectivity for formic acid of various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Time(h)</th>
<th>H(_2) ((\mu)mol)</th>
<th>CO(_2) Reduction ((\mu)mol)</th>
<th>HCOOH ((\mu)mol)</th>
<th>Selectivity HCOOH%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UIO-66-NH(_2)</td>
<td>4</td>
<td>2.90</td>
<td>4.80</td>
<td>1.84</td>
<td>38.3</td>
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<td></td>
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</tr>
<tr>
<td><strong>UIO-66-NH$_2$/1 wt% CNTs</strong></td>
<td></td>
<td>4</td>
<td>2.50</td>
<td>9.24</td>
<td>5.72</td>
</tr>
<tr>
<td><strong>UIO-66-NH$_2$/2 wt% CNTs</strong></td>
<td></td>
<td>4</td>
<td>2.00</td>
<td>28.8</td>
<td>18.2</td>
</tr>
<tr>
<td><strong>UIO-66-NH$_2$/3 wt% CNTs</strong></td>
<td></td>
<td>4</td>
<td>2.10</td>
<td>18.7</td>
<td>11.3</td>
</tr>
<tr>
<td><strong>UIO-66-NH$_2$/4 wt% CNTs</strong></td>
<td></td>
<td>4</td>
<td>3.81</td>
<td>16.1</td>
<td>9.41</td>
</tr>
<tr>
<td><strong>UIO-66-NH$_2$/5 wt% CNTs</strong></td>
<td></td>
<td>4</td>
<td>5.85</td>
<td>9.32</td>
<td>5.22</td>
</tr>
</tbody>
</table>

### 3.6 Electrochemical analysis and Time-resolved PL spectra tests

The charge transfer properties are further demonstrated by a series of measurements. As shown in Fig. 7(a), the photocurrent responses of different samples were measured under visible-light ($\lambda > 400$ nm) irradiation at a constant potential of 0.5 V (vs. SCE). The UIO-66-NH$_2$/2 wt% CNTs composite possesses enhanced light currents, indicating that the composite photocatalyst can utilize more photoinduced electrons, thus exhibiting superior CO$_2$ photoreduction activity. It was superior than the UIO-66-NH$_2$/2 wt% CNTs sample obtained through the mechanical mixing method (Fig. S7(a)). These results demonstrated that the hydrothermal method induced the samples display a higher photocurrent intensity, which indicated a strong visible-light absorption capability and low rate of recombination of photogenerated electron-hole pairs.

To get a deeper understanding of the changes in the conductivity of different samples, electrochemical impedance spectroscopy (EIS) measurements were performed in Fig. 7(b). Electrical equivalent circuits are determined to explain charge transfer processes occurring in the photocatalysis system, the sample of UIO-66-NH$_2$/2 wt% CNTs exhibited a smaller capacitance arc than the pure UIO-66-NH$_2$, implying that the introduction of CNTs could enhance the electron mobility by reducing the recombination of photogenerated electron-hole pairs of UIO-66-NH$_2$,
improve the conductivity of the materials and reduce the compound rate of the photovoltaic carrier. It was also smaller than the mechanical mixing sample (Fig. S7(b)), the advantages of hydrothermal synthesis is further demonstrated. These results indicate that the composite photocatalysts are active for reducing CO₂ at ambiance conditions with superior photocatalytic performance. The enhanced photocatalytic performance may be caused by the effective interfacial charge transfer between UIO-66-NH₂ and CNTs through the heterojunction which is evidenced in Fig. 7(c), the Time-resolved PL spectra decays reveal the average lifetime of UIO-66-NH₂(0.642 ns) and UIO-66-NH₂/2 wt% CNTs(0.924 ns). UIO-66-NH₂/2 wt% CNTs shows an increased long (τ₁), short (τ₂), and increased intensity-average (τ) PL lifetimes in comparison to UIO-66-NH₂, further verified that the introducing of CNTs can effectively suppress the charge recombination and elongate the lifetime of charge carriers[72]. Moreover, the longer PL lifetime of composites confirms the fast transfer of electrons from UIO-66-NH₂ to CNTs, thus suppressing the recombination of photogenerated electron-hole pairs and improve the photocatalytic performance.

3.7 Discussion of possible mechanism analysis

Based on the above experiments and results, a possible mechanism for the high photocatalytic activity of CO₂ reduction and selectivity of HCOOH over composites has been proposed(Fig. S8).
The enhancement of the photocatalytic activity and selectivity of combining the UIO-66-NH$_2$ and CNTs can be attributed to the following reasons: (1) UIO-66-NH$_2$ has a large surface area and pore capacity which provide more adsorption sites and photocatalytic reaction centers. This led to superior adsorption of CO$_2$ and improvement of the photocatalytic selectivity. (2) CNTs can improve the dispersion of MOFs and have excellent electronic conduction performance. The composites have large surface area which is also benefit to absorb the sacrificial reagent and thus capture and consume the holes effectively in the photocatalytic system. Besides, a newly Schottky barriers formed at the contact interface between the UIO-66-NH$_2$ and CNTs, which could act as electron trapping centers and thus separate the photogenerated electron-hole pairs. The electrons migrate to the interface and thus the interface could act as a reduction site due to the rich electrons, which could facilitate the reduction of CO$_2$, the formed heterostructures could harvest visible light energy and facilitate photocatalytic reactions at lower energies. The composites notably enhance both the photocatalytic activity of CO$_2$ reduction and selectivity of HCOOH [73].

4. Conclusion

In summary, we have successfully prepared UIO-66-NH$_2$/2 wt% CNTs samples with the hydrothermal method, which improved photocatalytic performance in the photoreduction of CO$_2$. This is due to the efficient visible light absorption derived from the loading of CNTs which is beneficial to inhibit the combination of electrons and holes. In addition, UIO-66-NH$_2$ has a large surface area and pore capacity which provide more adsorption sites and photocatalytic reaction centers. This leads to superior adsorption of CO$_2$, therefore improve the photocatalytic selectivity. When the loading amount of CNTs reached to 2 wt%, the reduction of CO$_2$ and the selectivity of HCOOH reach a maximum of 28.8 μmol and 63.1% respectively. Tight junction between
UIO-66-NH₂ and CNTs may serve as electron transfer bridges for accelerating electrons transfer from UIO-66-NH₂ to the interaction surface between the UIO-66-NH₂ and CNTs. Such a design idea of photocatalyst provided a promising method to fabricate highly efficient photocatalytic materials for CO₂ reduction.

Acknowledgments

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References:


