Compositing nanoparticles photo-catalyst with enormous surface areas metal–organic framework (MOF) will greatly improve photocatalytic performances. Herein, WO₃ nanoparticles are partly embedded into pores of MIL-101 or only supported on the outside of representative MIL-101, which were defined as embedded structure WO₃@MIL-101@WO₃ and coating structure WO₃&MIL-101 respectively. Different pH, concentration and loading percentage were researched. XRD, TEM and BET were carried to analyze the composites. Compared with the pristine WO₃, all WO₃ loaded MOF nanocomposites exhibited remarkable enhancing for the efficiency of photocatalytic degradation methylene blue under visible light. Their activity of the same loading percentage WO₃ in embedded structure and coating structure have increased for 9 and 3 times respectively compared with pure WO₃. The WO₃@MIL-101@WO₃ has 3 times higher efficiency than WO₃&MIL-101, because the shorter electron-transport distance can make a contribution to electron–hole separation. The further mechanism involved has been investigated by radical quantify experiment, XPS and photoluminescence spectroscopy.

Semiconductor nanoparticles are considered to be a superior photo catalyst for completely eliminating hazardous wastes and toxic contaminants caused by urbanization and industrialization because of their high photocatalytic activity and strong quantum-size effect. However, the properties of some semiconductors are ultraviolet light absorbing consisting only 4% among the whole solar energy, and have a tendency to aggregate, the two defects limited the photo catalyst’s universal usage. So, minimizing the particle size and exploring wide light spectrum catalyst have been a hot topic in the photo catalyst research. One of visible light absorbing photo catalyst WO₃ has become a fiercely debated material owing to the following advantages: (1) it is very stable, non-toxic and economic to synthesize which can be recycled and commonly used; (2) it can absorb visible spectrum light consisting 43% solar energy with a narrow band gap (2.7 eV); (3) suitable band alignment with a relatively positive valence band position allows its strong oxidation degradation effect.

However, pure WO₃ has a low photocatalytic performance. Some methods have been tried to solve these problems, such as synthesize WO₃ quantum dots to minimize the particle size, loading WO₃ with Pt nanoparticles to enhance the electrons transferring. Up to now, the problems cannot be solved thoroughly. Some MOFs have appeared as potential candidates for photo catalysis because of their high surface areas, tunable porosity, crystalline open structures and multi-functionalities. Due to their enormous inner surface, total surface area as much as 2000 times larger compared with silicon and grapheme which are usually used as carrier material in the catalyst field according to previously reports. As reported, MOFs have been found to be ideal materials for dispersing metal and semiconductor nanoparticles because their high surface area can avoid the aggregation of nanoparticles. Besides, the large specific surface area of MOFs also can supply a plenty of active adsorption sites and photocatalytic reaction centers, which would enhance the photocatalytic properties. The special structure of MOFs composited with organic ligands and metal ions allow the metal center acting as the shallow electron trap during the process of electrons transportation. The synergistic effect between MOFs and semiconductor can promote the charge separation and enhance the photocatalytic activity.

Particularly, many researchers have reported on MOFs based hetero structure photo-catalyst. Au@CdS@MIL-101, Co@MIL-101, Pd@MIL-101 and Pt@MIL-101 (Cr) have been investigated. But most of which are loaded photo-catalyst on surface of MIL-101, the large inner area of the pores cannot be used fully.

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In this paper, we synthesized WO₃ embed into the pores of MIL-101, and researched its photocatalytic properties, then compared with pure WO₃ and only coating outside MIL-101. Different pH, concentration and loading percentage were researched to boost the photocatalytic activity. Compared with WO₃&MIL-101 and pure WO₃, the photocatalytic efficiency of the embedded structure has improved 9 and 3 times respectively, and the pore size distribution and adsorption-desorption isotherm demonstrated that the WO₃ nanoparticles have embedded into the pores of MIL-101. The mechanism has been studied by trapped the active species hydroxyl radicals.

Experimental
Reagents and chemicals. All the chemicals were purchased from commercial sources and were utilized without further purification. Sodium tungstate and Terephthalic acid were applied by Aladdin Reagent Co. Ltd. Hydrochloric acid (HCl, 37%), Hydrofluoric acid (HF, 49%), Hydrogen peroxide (H₂O₂, 30%), Dimethyl formamide (DMF > 99.8%), Anhydrous ethanol, Chromic nitrate, were obtained from Sinopharm Chemical Reagent Co. Ltd. China. The solvent is water and is Ultra purified (18 MΩ·cm).

Synthesis of MIL-101. The MIL-101 was prepared via a hydrothermal method according to literature with slight modification²⁷. Commonly, 0.8 g Cr(NO₃)₃·9H₂O, 100 μL hydrofluoric acid (40%), 800 mg p-phenallic acid were put in 12.5 mL H₂O solvent. The system was ultrasonic under room temperature continued 30 min then transformed into 25 mL autoclave and maintained at 220 °C for 8 h. After cooling to room temperature, the resultant solid was isolated by filtration and rinsed with DMF and ethanol several times to remove remained substances, treated solvothermal with ethanol at 100 °C for 12 h, collected by filtration, dried at 80 °C, vacuum dried under 20 °C.

Synthesis of WO₃&MIL-101. In order to deposit WO₃ completely outside of MIL-101, direct settlement method was used and with MIL-101 not being degassed. With the same steps to prepare WO₃ precursor, then 100 mg not degassed MIL-101 was added to the solution, stirring for 30 min, the temperature was raised to 120 °C for 12 h, collected by filtration, dried at 80 °C, vacuum dried at 150 °C and then stored for further use.

Synthesis of WO₃@MIL-101@WO₃. Different sodium tungstate quality, pH and concentration were investigated, the different condition were listed as Table S1. Typically, 320μL hydrochloric acid which was diluted to 5 mL with water, then 10 mg sodium tungstate was dissolved in 40 mL water was added. After adding 100 μL hydrogen peroxide, the mixture was stirred for 30 min. Then 100 mg MIL-101 was added to the solution, stirring for 24 h under room temperature. Then the mixture was stirring and heated with oil bath by stepwise warming method. After temperature raised to 30 °C, it was kept at 30 °C for 1 h. Then raise the temperature to 45 °C and keep it for 1 h. After that it was raised to 60 °C and kept for 3 h, the temperature was raised to 120 °C until the water was dried up. The substance was washed with water and ethanol several times.

Characterization. The crystal structure of the prepared samples were characterized by a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Kα1 irradiation (λ = 0.15406 nm) under 40 kV and 40 mA. XPS diffraction patterns were carried out by an Axis-His spectrometer (Kratos Corporation) with a Mg Kα X-ray source, and the spectra were adjusted to the C 1s peak at 284.8 eV. The shape and size of the nanocomposites were characterized by a JEO JEM-6700F field emission scanning electron microscope with an accelerating voltage of 20kV, respectively. TEM and HRTEM images were obtained under a JEM-2100 transmission electron microscope with an accelerating voltage of 20kV. The surface area and the pore size distribution were measured on Quantachrome Autosorb-IQ sorption system at 77 K. Optical absorption properties (DRS) were detected under a Shimadzu UV-3600 spectrometer with a reference of BaSO₄. The photoluminescence (PL) emission spectra of samples were observed on a Hitachi F-4500 luminescence spectrometer.

Photo Catalytic Activity Test. The photocatalytic degradation performance of Methylene Blue (MB) test was carried out under visible light irradiation⁴⁴. A xenon lamp (300 W) with visual light filter was dispersed in an aqueous solution (50 mL) containing 30 mg/L MB dye by ultrasonic treatment for 5 min and maintained stirring for 30 min. Then, the solution was transferred to a quartz reaction vessel and agitated for some time. A liquid (5 mL) was sampled at scheduled irradiation time and the suspended catalyst were eliminated by centrifugation under 8000 rpm for 5 min. The UV-Visible absorption spectrum of the solution was carried out with a UV-Visible absorption spectrum of the solution was carried out with a UV-Vis spectrophotometer (UV-3600). The percentage of degradation was defined as $-\ln (C/C_0)$, herein, C₀ refers the absorption ($\lambda_{max} = 664$ nm) of MB solution prior irradiation and C indicates the absorption of MB solution at each irradiated time interval.

Active Species Trapping and Superoxide Radical Quantification Experiments. For detecting the active species during photocatalytic reactivity⁴⁴, hydroxyl radicals (·OH), the superoxide radical (O₂⁻·), and holes (h⁺) were trapped by adding 2.0 mM (according to the reaction system) IPA⁴⁶ (a quencher of ·OH), AgNO₃⁴⁷ (a quencher of O₂⁻·), and TEOA⁴⁸ a quencher of h⁺ respectively. The method was similar to the former photocatalytic activity test⁴⁴. TA (5 × 10⁻⁴ M in a 2 × 10⁻¹ M NaOH solution), which reacts readily with ·OH generating from WO₃&MIL-101 and WO₃@MIL-101@WO₃. The production of ·OH was quantitatively analyzed by detecting the concentration of 2-hydroxyterephthalic acid (fluorescence peak at about 425 nm by excitation with the wavelength of 315 nm) with Shi-madzu spectro fluorophotometer (RF-5301 pc) after centrifugation⁴⁷. The method was similar to the former photocatalytic activity test, with TA replacing the MB⁴⁸.
Results and Discussion

Reaction Process Illustration. As shown in Fig. 1, the WO₃@MIL-101@WO₃ hetero-structure were synthesized by low temperature H₂O₂ assistant sol-gel method. The process of adding H₂O₂ was very important for the formation of peroxo-tungstate gel precursor, obvious Tyndall effect can be observed. Stirring for 24 h giving enough time for the slow kinetic reaction process of MIL-101 dipping into peroxo tungstate gel. The loading percentage, pH and concentration influencing the properties of precursor were also researched listed in Table S1.

The resultant WO₃&MIL-101 and WO₃@MIL-101@WO₃ samples have been well characterized by various techniques. The actual loading percentages tungsten (5%-15%) at various precursor concentrations determined by atomic absorption spectrum (AAS) method matches well with the theoretical loading (5.27–15.5%), as shown in Table S2, indicating that the H₂O₂ assistant sol-gel method is effective in loading WO₃ into MIL-101.

Structure, composition, and microstructure. As shown in Fig. 2a, the crystal structure of MIL-101 is in good agreement with the literature reported⁴¹, demonstrating the formation of MIL-101 with ultrapure and good crystallinity. After loading WO₃, the characteristic XRD peaks of MIL-101 in all samples are maintained, demonstrating the treatment did not have the damage on the crystal structure of MIL-101. The weaker peaks of WO₃@MIL-101 and WO₃@MIL-101@WO₃ samples have been well characterized by various techniques. The actual loading percentages tungsten (5%-15%) at various precursor concentrations determined by atomic absorption spectrum (AAS) method matches well with the theoretical loading (5.27–15.5%), as shown in Table S2, indicating that the H₂O₂ assistant sol-gel method is effective in loading WO₃ into MIL-101.

The survey pattern of WO₃, WO₃@MIL-101@WO₃, and MIL-101 was shown in Fig. 3a. The high resolution XPS of O element (Fig. 3b) show the position 530.6 eV for WO₃@MIL-101@WO₃ which has right shift 0.21 eV compared with WO₃, the absorbed oxygen at 532.67 eV was disappeared, indicating the O element has some changes in WO₃@MIL-101@WO₃ compared with pure WO₃. Figure 3c,d show the binding energy shift and half band width changes, W₄f2/7 and W₄f2/5 have right shift 0.12 eV and 0.13 eV, respectively. The half band width of WO₃@MIL-101@WO₃ has been widen 0.44 eV compared with WO₃, these results all show that W element has a good attachment with the linkages of MIL-101, there are interactions between WO₃ and MIL-101.
In order to further detect the relation of WO₃ and MIL-101, DLS method was adapted. In Table S3, the zeta potential of WO₃, WO₃&MIL-101, WO₃@MIL-101@WO₃ and MIL-101 are −34.1 mV, −8.69 mV, −6.04 mV and 34.5 mV respectively. The result for WO₃&MIL-101 (−8.69 mV) and WO₃@MIL-101@WO₃ (−6.04 mV) shows electrostatic attraction between MIL-101 and oppositely charged WO₃. A close interaction of the WO₃&MIL-101 and WO₃@MIL-101@WO₃ composite can be achieved with the electrostatic attraction. The more negative potential of WO₃&MIL-101 than WO₃@MIL-101@WO₃ indicates there exist more WO₃ nanoparticles on the surface of MIL-101.

As shown in Fig. 4a, octahedral structure with smooth surface of MIL-101 have the size of 400 nm–600 nm. As shown in Fig. 4b, the size of pure WO₃ nanosheets are about 50 nm in thickness and 400 nm in width. After loading WO₃, the surface of MIL-101 became rough and coating a slice WO₃ on the surface of MIL-101 for WO₃@MIL-101@WO₃. For WO₃&MIL-101, WO₃ particles growth and there are intensity aggregating together with each other. The average particle size is about 40 nm shown as Fig. S2d. For the exploration experiment, we investigated the WO₃&MIL-101@WO₃ samples with different WO₃ loading proportion (5–15%), different pH, different concentration and not adding hydrogen peroxide and the SEM results are displayed in Figs S2 and S3, and S4. As can be seen from Fig. S2, WO₃ were thinly well coating on MIL-101 much like the morphology of WO₃@MIL-101@WO₃, as the loading proportion increasing, the amount of WO₃ slice increase. Figure S2c show no hydrogen peroxide added in the solution, WO₃ nanoparticles have grown much larger, indicating that the adding hydrogen peroxide can change the state of peroxo tungstate precursor gel, which is very important for WO₃ embed into the pores of MIL-101. As can be seen Figs S3 and S4 in all WO₃@MIL-101@WO₃ samples, WO₃ are all well slice coating outside MIL-101, with pH and concentration changes, the state of WO₃ have some difference.

In order to study the morphology of MIL-101 (Fig. 5a, insert), TEM and HRTEM measurements were carried. The images of WO₃@MIL-101@WO₃ and WO₃&MIL-101, MIL-101, WO₃ were shown in Fig. 5. The insert picture shows a typical octahedral structure of MIL-101 which have an average size of 500 nm. In the WO₃@MIL-101@WO₃ sample, WO₃ was very little and well coating outside MIL-101, in WO₃&MIL-101 sample, WO₃ nanoparticles with a small size are well dispersed outside of MIL-101 without obvious aggregation, demonstrating that the MIL-101 can well hindering the growth of WO₃ as an excellent matrix. Displayed by the HRTEM images of WO₃@MIL-101@WO₃ and WO₃&MIL-101, the marked lattice pitch of 0.536 nm and 0.46 nm on the surface of MIL-101 is corresponded to the (020) and (011) planes of WO₃, and the marked lattice pitch of 0.346 nm and 0.256 nm on the shell is matched with the (111) and (002) planes of WO₃. These results suggest that an intimate contact which will be helpful for the charge separation and transferring between WO₃ and MIL-101. The energy dispersive X-ray spectroscopy (EDS) mapping (Fig. S5) was conducted to further confirmed the component and
structure of WO$_3$@MIL-101@WO$_3$, the crystal structure of MIL-101 can be displayed by the uniform Cr elements in the background$^{27}$.

To clarify the location of WO$_3$ relative to MIL-101, the N$_2$ adsorption measurement of MIL-101 was carried which shows type I property with secondary uptakes at p/p$_0$ of around 0.1 and 0.2 (Fig. 6a), which is a typical MIL-101 adsorption curve$^{50,51}$. After loading WO$_3$ nanoparticles, the adsorption-desorption isotherm of WO$_3$&MIL-101 sample has little changes but the adsorption-desorption isotherm of WO$_3$@MIL-101@WO$_3$ has a significant change compared with MIL-101 and WO$_3$&MIL-101 and N$_2$ adsorption decreased with the WO$_3$ content increased. The surface area of MIL-101 was measured to be 2480 m$^2$/g and the total pore size value was estimated to be 1.193 cm$^3$/g at a relative pressure of 0.99 (shown in Table 1), both are similar to the numbers reported in the literature. The surface area of WO$_3$&MIL-101 was 2350 m$^2$/g and pore size value was 1.153 cm$^3$/g, both are close to MIL-101. The surface area of WO$_3$@MIL-101@WO$_3$ samples gradually decreased from 1668 to 1255 m$^2$/g, the pore size value change from 0.835 to 0.651 cm$^3$/g, as WO$_3$ content increased from 5% to 15%. The pore size distribution is shown in Fig. S7, the pore size at 1.8, 2.6 and 3.2 nm are attributed to pure MIL-101, which has been reported in literature$^{50}$, compared with pure MIL-101, the pores size distribution of the WO$_3$&MIL-101 have little changes while the pore size of WO$_3$@MIL-101@WO$_3$ have a significantly decrease than both pure MIL-101 and WO$_3$&MIL-101. With the WO$_3$ content increased, the pore size shows a decreasing trend. All these phenomena could be caused by WO$_3$ embed into the pores of MIL-101. The results suggest that the WO$_3$ nanoparticles in WO$_3$@MIL-101@WO$_3$ samples are successfully embedded in the cavities of MIL-101. WO$_3$ nanoparticles have little influence for surface area and pore size of MIL-101, so WO$_3$ nanoparticles are possibly on the surface of MIL-101 in WO$_3$&MIL-101 sample.

Combined with the TEM and SEM results, it can be concluded the WO$_3$ particles just coat on the surface of MIL-101 in WO$_3$&MIL-101 sample. The WO$_3$ particles partly embed into the pores and partly on the surface of MIL-101 in WO$_3$@MIL-101@WO$_3$.

**UV-Vis DRS analysis.** UV-Vis DRS spectra were used to analyze the optical properties of the MIL-101 and the different WO$_3$ loading proportion samples (Fig. 7). MIL-101 exhibits two characteristic absorption band centered at 450 nm and 600 nm, which coincides with that in literature$^{27}$. The band of pure MIL-101 in the UV region belongs to $\pi-\pi^*$ transitions of ligands and the bands in the visible region can be assigned to the D-D spin-allowed transition of the Cr$^{3+}$. WO$_3$ displays a sharp fundamental absorption edge rise at 475 nm as expected, corresponding to a band gap of 2.75 eV$^7$. Compared with that of MIL-101, the WO$_3$@MIL-101@WO$_3$ composite shows an enhanced band absorption in visible light region, this may correspond to the visible light enhanced of WO$_3$. Compared with that of pure WO$_3$, WO$_3$@MIL-101@WO$_3$ composite shows an absorption band centered at 600 nm, which is attributed to the absorption of MIL-101 matrix.

**Photocatalytic Degradation of Organic Pollutant.** The MIL-101 loading WO$_3$ samples were evaluated for photocatalytic MB degradation. As shown in Fig. 8a, comparing with pure WO$_3$, the embedded structure
WO₃@MIL-101@WO₃ and coating structure WO₃&MIL-101 increased 9 times and 3 times, respectively, due to the closely contact between WO₃ and MIL-101 which can be concluded from XPS and DLS data. Also, the embedded structure has 3 times higher efficiency than coating structure due to the part of WO₃ have embedded into the pores of MIL-101 resulting in the shorter distance of the electrons transfer from WO₃ to MIL-101 comparing with coating structure. Figure 8b show the degradation efficiency of different loading percentages and a series of control experiment, which shown 10% WO₃ loading sample has the best photocatalytic efficiency. From the control experiment, it can be seen that pure MIL-101 has no photocatalytic efficiency, MB cannot be degraded by self-sensitization and the light are the necessary condition during photocatalytic. Different pH and concentration

Figure 5. (a) TEM image of (10%) WO₃@MIL-101@WO₃ (insert was pure MIL-101), (b) HRTEM image of (10%) WO₃@MIL-101@WO₃ and the reflection of crystal face about its inverse FFT, (c) TEM image of (10%) WO₃&MIL-101 (insert was pure MIL-101), (d) HRTEM image of (10%) WO₃&MIL-101 and the reflection of crystal face about its inverse FFT.

Figure 6. BET adsorption–desorption isotherm of MIL-101, (10%) WO₃&MIL-101 and different loading percentage of WO₃@MIL-101@WO₃.
were also investigated in Fig. S8a,b which shown that pH and concentration influence the photocatalytic efficiency of MB degradation. The WO₃@MIL-101@WO₃ has the best photocatalytic efficiency when the amount of HCl was 280 μL and the volume of water was 35 mL.

**Mechanism Investigation on Photocatalytic Performance Improvement.** To further unveil the higher photocatalytic efficiency of WO₃@MIL-101@WO₃ than WO₃&MIL-101, photocurrent measurement have been carried and the results show that the photocurrent for both MIL-101 supported WO₃ get enhanced as compared to the pristine WO₃ (Fig. 9a), revealing that the formation of WO₃-MOF schottky junction helps to separate the photo-generated electron-hole pairs⁵². The WO₃@MIL-101@WO₃ displays much stronger photocurrent response than WO₃&MIL-101, suggesting the much higher efficiency of the charge transfer⁵². This result is also supported by the photoluminescence (PL) emission spectroscopy, which provides useful hints for the photo-excited charge transfer and recombination. The PL intensity is slightly weakened when the WO₃ only coating outside MOF, while get greatly suppressed when some WO₃ nanoparticles have dispersed inside

| Sample                  | BET Surface area (m²/g) | Pore size Volume (cm³/g) |
|-------------------------|-------------------------|--------------------------|
| MIL-101                 | 2480                    | 1.193                    |
| (10%) WO₃&MIL-101       | 2450                    | 1.153                    |
| (5%) WO₃@MIL-101@WO₃    | 1668                    | 0.835                    |
| (10%) WO₃@MIL-101@WO₃   | 1360                    | 0.678                    |
| (15%) WO₃@MIL-101@WO₃   | 1255                    | 0.651                    |

Table 1. The surface area and pore size volume of MIL-101, (10%) WO₃&MIL-101 and different loading percentage of WO₃@MIL-101@WO₃.
the MOF (Fig. 9b). These observations indicate that the irradiative electron-hole recombination is more effectively suppressed by extracting the electrons from internal WO3 than coating WO3.53. Such distinctly different photoelectrochemical properties in WO3@MIL-101@WO3 and WO3&MIL-101 unambiguously demonstrate that the part of WO3 in the pores of MIL-101 contribute mostly of the photocatalytic efficiency of MB degradation. For comparison, we also investigated the photoluminescence (PL) emission spectroscopy of different WO3 loading percentage (Fig. S9), the PL intensity are corresponding with the photocatalytic efficiency. The WO3 loaded MOF samples all have lower intensity than pure WO3, pure MIL-101 have a lower photoluminescence emission. It indicated that WO3-MOF schottky junction can well suppressed the electron-hole pairs recombination and pure MIL-101 cannot be excited by visible light. In order to further investigate the migration and interface transfer or recombination rates of charge carriers electrochemical impedance spectra (EIS) was detected in Fig. S10. It was found that the WO3@MIL-101@WO3 and WO3&MIL-101 composite exhibits much smaller arc sizes than the pure WO3 under visible light irradiation. It demonstrates that the heterojunction composite has faster electron transfer through an intimated interface between MIL-101 and WO3 as compared to the pristine WO3, which is in good agreement with the photocatalytic performance.

The photocatalytic mechanism of WO3@MIL-101@WO3 have been researched by active species trapping and ·OH quantify experiment during the photocatalytic process.48 In order to study the active species of the photocatalytic reaction of WO3@MIL-101@WO3, the trapping experiment was investigated and showed in Fig. 10a. It can be concluded that the addition of AgNO3 (a quencher of e−, which can hinder the formation of O2−) have no influence on photocatalytic degradation of MB. On the contrary, the addition of IPA (a quencher of ·OH) or TEOA (a quencher of h+) have an obvious influence of decrease on the photocatalytic degradation of MB. Therefore, the conclusion can be drawn that photo-generated holes (h+) and ·OH are the main effective species on MB degradation for WO3@MIL-101@WO3 under visible light irradiation. The result consistent with the kind of effective species of pure WO3 and WO3&MIL-101. It can be concluded that the kind of active species have not changed after the combined. ·OH production quantification experiments have been revealed by the fluorescent intensity of TAOH for WO3, WO3&MIL-101 and WO3@MIL-101@WO3 in Fig. 10b. For WO3&MIL-101, the produce of ·OH just have little changed compared with pure WO3. But for WO3@MIL-101@WO3 the fluorescent intensity of TAOH compared with pure WO3 were totally different, there has a significant increase of ·OH. Above result can be explained: the electron produced from WO3 conduction band can be easily recombined due to the
positive conduction level because of rapidly recombination of electron-hole pairs, so there are little ·OH produced for WO₃. For WO₃&MIL-101, because of the similar ·OH quantify result and the result of PL and photocurrent, the mechanism is the same as pure WO₃. This can be explained that WO₃ coating outside of MIL-101 only, nanoparticles are tending to be aggregating and electrons are favoring to be stacking and recombination rate increase. For WO₃@MIL-101@WO₃ the electrons produced from conduction band of WO₃ transferred to MIL-101 due to the shorter electrons transfer distance. Due to the transformation of electrons, the holes can be separated to a greater degree, as a result, ·OH can be easily produced from high valence position of h⁺.

This may also conclude that WO₃ in the pores of MIL-101 have a shorter distance to transfer electrons from WO₃ conduction band resulting in higher electrons-hole separation efficiency comparing with WO₃&MIL-101, the same conclusion have been shown in the literature⁵². It may be the reason the embedded structure has higher efficiency than coating structure. The possible photocatalytic mechanism of WO₃@MIL-101@WO₃ and WO₃&MIL-101 were shown in Figs 11 and 12.

**Figure 11.** The possible photocatalytic mechanism scheme of WO₃@MIL-101@WO₃ under visible light irradiation (λ ≥ 420 nm).

**Figure 12.** The possible photocatalytic mechanism scheme of WO₃&MIL-101 under visible light irradiation (λ ≥ 420 nm).
Conclusion

The WO₃@MIL-101@WO₃ and WO₃&MIL-101 hetero-structure were successfully synthesized, the WO₃ nanoparticles were successfully embedded into the pores of MIL-101. MIL-101 can confine the particle size of WO₃ and improve the nanoparticles from aggregation and leaching to result in the enhancement of photo activity. Different loading percentage, pH and concentration were investigated to boost the photocatalytic degradation of MB, a great enhancement in photocatalytic activity is 10% content embedded structure sample, which increased 9 times activity compared with pure WO₃ and 3 times compared with WO₃&MIL-101. The photocatalytic mechanism of WO₃@MIL-101@WO₃ were investigated. Photocurrent, PL and -OH quantify experiment all show that when WO₃ embedded into the pores of MIL-101, MIL-101 can play the role of promoting charge separation due to the short distance improving the electron-hole separation efficiency. The synthesis strategy presented here can be expended as a facile approach to synthesizing related dipping metal oxide into the pores of metal-organic framework for functional design and application.

References

1. Luo, X. et al. Facile One-Step Synthesis of Inorganic-Framework Molecularly Imprinted TiO₂/WO₃ Nanocomposite and Its Molecular Recognitive Photocatalytic Degradation of Target Contaminant. Environ. Sci. Technol. 47, 7404–7412 (2013).
2. Seifollahi Bazargani, M. et al. Visible Light Photocatalysis with c-WO₃ - x/WO₃ + H₂O Nanoheterostructures In Situ Formed in Mesoporous Polycarboxylate-Siloxane Polymer. J. Am. Chem. Soc. 135, 4467–4475 (2013).
3. Liu, R. et al. Water Splitting by Tungsten Oxide Prepared by Atomic Layer Deposition and Decorated with an Oxygen-Evolving Catalyst. Angew. Chem. Int. Ed. 123, 519–522 (2011).
4. Grigioni, I., Stampapecskoe, K. G., Sellì, E. & Kamat, P. V. Dynamics of Photogenerated Charge Carriers in WO₃/BiVO₄ Heterojunction Photoanodes. J. Phys. Chem. C 119, 20792–20800 (2015).
5. Bi, D. & Xu, Y. Improved Photocatalytic Activity of WO₃ through Clustered Fe₂O₃ for Organic Degradation in the Presence of H₂O₂. Langmuir 27, 9359–9366 (2011).
6. Luan, J., Shen, Y., Li, Y. & Paz, Y. The Structural, Photocatalytic Property Characterization and Enhanced Photocatalytic Activities of Novel Photocatalysts Bi₃GaSbO₅ and Bi₂InSbO₅ during Visible Light Irradiation. Materials 9 (2016).
7. Wenderich, K., Klaassen, A., Siretanu, I., Mugele, F. & Mul, G. Sorption-Determined Deposition of Platinum on Well-Defined Platelike WO₃. Angew. Chem. Int. Ed. 53, 12476–12479 (2014).
8. Pesci, F. M., Cowan, A. J., Alexander, B. D., Durrant, J. R. & Klug, D. R. Charge Carrier Dynamics on Mesoporous WO₃ during Water Splitting. J. Phys. Chem. Lett. 2, 1900–1903 (2011).
9. Arutanti, O., Nandyanto, A. B. D., Ogi, T., Kim, T. O. & Okuyama, K. Influences of Porous Structurization and Pt Addition on the Improvement of Photocatalytic Performance of WO₃ Particles. ACS Appl. Mater. Interfaces 7, 3009–3017 (2015).
10. Jeon, D., Kim, N., Bae, S., Han, Y. & Ryu, J. WO₃/Conducting Polymer D. Kim, Heterostructured Photoanodes for Efficient and Stable Photoelectrochemical Water Splitting. ACS Appl. Mater. Interfaces 10, 8036–8044 (2018).
11. Li, Y., Tang, Z., Zhang, J. & Zhang, Z. Defect Engineering of Air-Treated WO₃ and Its Enhanced Visible-Light-Driven Photocatalytic and Electrochemical Performance. J. Phys. Chem. C 120, 9750–9763 (2016).
12. Kim, J., Lee, C. W. & Choi, W. Platinum-WO₃ as an Environmental Photocatalyst that Generates OH Radicals under Visible Light. Environ. Sci. Technol. 44, 6849–6854 (2010).
13. Xi, G. et al. Ultrathin W₆O₁₈ Nanowires with Diameters below 1 nm: Synthesis, Near-Infrared Absorption, Photoluminescence, and Photocatalytic Reduction of Carbon Dioxide. Angew. Chem. Int. Ed. 51, 2395–2399 (2012).
14. Xi, G. et al. In Situ Growth of Metal Particles on 3D Urchin-Like WO₃ Nanostructures. J. Am. Chem. Soc. 134, 6508–6511 (2012).
15. Zhao, Z. G. & Miyachi, M. Nanoporous-Walled Tungsten Oxide Nanotubes as Highly Active Visible-Light-Driven Photocatalysts. Angew. Chem. Int. Ed. 47, 7051–7055 (2008).
16. Ma, B., Guo, J., Dai, W.-L. & Fan, K. Ag-AgCl/WO₃ Hollow Sphere with Flower-Like Structure and Superior Visible Photocatalytic Activity. Appl. Catal. B 123–124, 193–199 (2012).
17. Ding, J. et al. Selective Deposition of Silver Nanoparticles onto WO₃ Nanorods with Different Facets: The Correlation of Facet-Induced Electron Transport Preference and Photocatalytic Activity. J. Phys. Chem. C 120, 4345–4353 (2016).
18. Bu, X., Chen, Z. & Sun, C. Highly Efficient Z-Scheme Ag₃PO₄/Ag/WO₃–x Photocatalyst for Its Enhanced Photocatalytic Performance. Appl. Catal. B 179, 363–371 (2015).
19. Xiang, Q. et al. Au Nanoparticle Modified WO₃ Nanorods with Their Enhanced Properties for Photocatalysis and Gas Sensing. J. Phys. Chem. C 114, 2049–2055 (2010).
20. Zhang, Q. et al. Light-Driven Au-WO₃@C Janus Micromotors for Rapid Photodegradation of Dye Pollutants. ACS Appl. Mater. Interfaces 9, 4674–4683 (2017).
21. Tomita, O., Otsubo, T., Higashi, M., Ohtani, B. & Ake, R. Partial Oxidation of Alcohols on Visible-Light-Driven WO₃ Nanoparticles Loaded with Palladium Oxide Catalyst. ACS Catal. 6, 1134–1144 (2016).
22. Yu, X. & Cohen, S. M. Photocatalytic Metal–Organic Frameworks for Selective 2,2,2-Trifluoroethylation of Styrenes. J. Am. Chem. Soc. 138, 12320–12323 (2016).
23. Zhang, Z.-M. et al. Photosensitizing Metal–Organic Framework Enabling Visible-Light-Driven Proton Reduction by a Wells–Dawson-Type Polyoxometalate. J. Am. Chem. Soc. 137, 3197–3200 (2015).
24. Xu, H.-Q. et al. Visible-Light Photoreduction of CO₂ in a Metal–Organic Framework: Boosting Electron–Hole Separation via Electron Trap States. J. Am. Chem. Soc. 137, 13440–13443 (2015).
25. Wang, R., Dong, X. Y., Du, J., Zhao, J. Y. & Zang, S. Q. MOF-Derived Bifunctional Cu₃P Nanoparticles Coated by a N,P-Codoped Carbon Shell for Hydrogen Evolution and Oxygen Reduction. Adv. Mater. 30 (2018).
26. Wu, Z. L. et al. A Semi-Conductive Copper–Organic Framework with Two Types of Photocatalytic Activity. Angew. Chem. Int. Ed. 55, 4938–4942 (2016).
27. Wang, Y. et al. Controlled Fabrication and Enhanced Visible-Light Photocatalytic Hydrogen Production of AuCdS/MIL-101 Heterostructure. Appl. Catal. B 185, 307–314 (2016).
28. Guan, R. Y., Yu, X. Y., Wu, H. B. & Lou, X. W. Complex Nanosstructures from Materials Based on Metal–Organic Frameworks for Electrochemical Energy Storage and Conversion. Adv. Mater. 29, 47 (2017).
29. Kim, D., Whang, D. R. & Park, S. Y. Self-Healing of Molecular Catalyst and Photosensitizer on Metal–Organic Framework: Robust Molecular System for Photocatalytic H₂ Evolution from Water. J. Am. Chem. Soc. 138, 8698–8701 (2016).
30. Gu, Y. et al. Controllable Modular Growth of Hierarchical MOF-on-MOF Architectures. Angew. Chem. Int. Ed. 56, 15658–15662 (2017).
31. Liang, Z., Qu, C., Xia, D., Zou, R. & Xu, Q. Atomically Dispersed Metal Sites in MOF-Based Materials for Electro catalytic and Photocatalytic Energy Conversion. Angew. Chem. Int. Ed. (2018).
32. Liu, H., Xu, C., Li, D. & Jiang, H. L. Photocatalytic Hydrogen Production Coupled with Selective Benzylamine Oxidation over MOF Composites. Angew. Chem. Int. Ed. 130, 5477–5481 (2018).
33. Ryu, U. et al. Nanocrystalline Titanium Metal–Organic Frameworks for Highly Efficient and Flexible Perovskite Solar Cells. ACS Nano 12, 4968–4975 (2018).
34. Zhang, X., Zhang, X., Johnson, J. A., Chen, Y.-S. & Zhang, J. Highly Porous Zirconium Metal–Organic Frameworks with 3-UH2-like Topology Based on Elongated Tetrahedral Linkers. J. Am. Chem. Soc. 138, 8380–8383 (2016).
35. Leng, F., Liu, H., Ding, M., Lin, Q.-P. & Jiang, H.-L. Boosting Photocatalytic Hydrogen Production of Porphyrinic MOFs: The Metal Location in Metalloporphyrin Matters. ACS Catal. 8, 4583–4590 (2018).
36. Wu, P. et al. Photoactive Chiral Metal–Organic Frameworks for Light-Driven Asymmetric α-Alkylation of Aldehydes. J. Am. Chem. Soc. 134, 14991–14999 (2012).
37. Wang, Y. et al. Hydroxide Ligands Cooperate with Catalytic Centers in Metal–Organic Frameworks for Efficient Photocatalytic CO2 Reduction. J. Am. Chem. Soc. 140, 38–41 (2018).
38. Liu, Y. & Tang, Z. Multifunctional Nanoparticle@MOF Core–Shell Nanostructures. Adv. Mater. 25, 5819–5825 (2013).
39. Nguyen, H. L. et al. A Titanium–Organic Framework as an Exemplar of Combining the Chemistry of Metal– and Covalent–Organic Frameworks. J. Am. Chem. Soc. 138, 4330–4333 (2016).
40. Wang, C., deKrafft, K. E. & Lin, W. Pt Nanoparticles@Photoactive Metal–Organic Frameworks: Efficient Hydrogen Evolution via Synergistic Photoexcitation and Electron Injection. J. Am. Chem. Soc. 134, 7211–7214 (2012).
41. Han, J. et al. Metal–Organic Framework Immobilized Cobalt Oxide Nanoparticles for Efficient Photocatalytic Water Oxidation. J. Mater. Chem. A 3, 20607–20613 (2015).
42. Li, H. et al. Palladium Nanoparticles Confined in the Cages of MIL-101: An Efficient Catalyst for the One-Pot Indole Synthesis in Water. ACS Catal. 1, 1604–1612 (2011).
43. Aijaz, A. et al. Immobilizing Highly Catalytically Active Pt Nanoparticles Inside the Pores of Metal–Organic Framework: A Double Solvents Approach. J. Am. Chem. Soc. 134, 13926–13929 (2012).
44. Tian, L., Ye, L., Deng, K. & Zan, L. TiO2/Carbon Nanotube Hybrid Nanostructures: Solvothermal Synthesis and Their Visible Light Photocatalytic Activity. J. Solid State Chem. 184, 1465–1471 (2011).
45. Ye, L. et al. Two Different Roles of Metallic Ag on Ag/AgX/BiOx (X = Cl, Br) Visible Light Photocatalysts: Surface Plasmon Resonance and Z-Scheme Bridge. ACS Catal. 2, 1677–1683 (2012).
46. Hao, Q. et al. One-Pot Synthesis of C/β-Bi2O3 Composite with Enhanced Photocatalytic Activity. Appl. Catal. B 219, 63–72 (2017).
47. Li, W. et al. Evidence for the Active Species Involved in the Photoinduced Process of Methyl Orange on TiO2. J. Phys. Chem. C 116, 3552–3560 (2012).
48. Ye, L., Liu, J., Jiang, Z., Peng, T. & Zan, L. Facets Coupling of BiOBr-g-C3N4 Composite Photocatalyst for Enhanced Visible-Light-Driven Photocatalytic Activity. Appl. Catal. B 142–143, 1–7 (2013).
49. Ye, L., Liu, J., Jiang, Z., Peng, T. & Zan, L. The Pure Shape Effect with A Removing Facet Effect of Single-Crystalline Anatase TiO2 (101) for Photocatalytic Application. Nanoscale 5, 9391–9396 (2013).
50. Rallapalli, P. B. S. et al. Activated Carbon @ MIL-101(Cr): A Potential Metal-Organic Framework Composite Material for Hydrogen Storage. Int. J. Energy Res. 37, 746–753 (2013).
51. Férey, G. et al. A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. Science 309, 2040 (2005).
52. Xian, J. D. et al. Boosting Photocatalytic Hydrogen Production of a Metal–Organic Framework Decorated with Platinum Nanoparticles: The Platinum Location Matters. Angew. Chem. Int. Ed. 55, 9389–9393 (2016).
53. Liu, L. et al. Exceptionally Robust In-Based Metal–Organic Framework for Highly Efficient Carbon Dioxide Capture and Conversion. Inorg. Chem. 55, 3558–3565 (2016).

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Author Contributions
I.W. and L.Z. supervised the project. L.W. designed and carried out all experiments. L.Z. helped to revise the final format of the article.

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