Post-synthetic modification of aluminum trimesate and copper trimesate with TiO₂ nanoparticles for photocatalytic applications

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ABSTRACT

Organic pollutants have been a significant source of concern in recent years due to their facile dissemination and harmful effects. In this work, two different metal–organic frameworks (MOFs) were initially prepared by hydrothermal treatment, namely aluminum trimesate (MIL-100(Al)) and copper trimesate (HKUST-1). These materials were subsequently submitted to a post-synthetic modification step to grow titania nanoparticles on their surface. Anatase nanoparticles with sizes around 5 nm were successfully anchored on MIL-100(Al), and the concentration of TiO₂ in this sample was about 68 wt.%. This is the first time that this composite (TiO₂@MIL-100(Al)) is reported in the literature. It showed an improved photocatalytic activity, removing 90% of methylene blue (k_app = 1.29 h⁻¹), 55% of sodium diclofenac (k_app = 0.21 h⁻¹), and 62% of ibuprofen (k_app = 0.37 h⁻¹) after four hours of illumination with UV-A light. A significant concentration (14 lM) of reactive oxygen species (ROS) was detected for this composite. HKUST-1 showed a structural collapse during its post-synthetic modification, leading to a non-porous material and providing fewer sites for the heterogeneous nucleation of titania. This behavior led to a low concentration of rutile nanoparticles on HKUST-1 (9 wt.%). However, the obtained composite (TiO₂@HKUST) also showed an improved photoactivity compared to HKUST-1, increasing the photodegradation rates evaluated for methylene blue.

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(0.05 h\(^{-1}\) vs. 0.29 h\(^{-1}\)), sodium diclofenac (negligible vs. 0.03 h\(^{-1}\)), and ibuprofen (0.01 h\(^{-1}\) vs. 0.02 h\(^{-1}\)). This work brings new insights concerning the preparation of photocatalysts by growing semiconductor nanoparticles on trimesate-based MOFs.

### Introduction

In recent decades, the contamination of the atmosphere, soil, and water by hazardous species has been a significant source of concern [1–3]. These pollutants can occur naturally in the environment, but their primary source is human activity [4]. The industrial sector plays a key role in this contamination due to accidents and incorrect waste disposal [5, 6]. However, civil society also contributes to this scenario mainly due to the incorrect disposal of pollutants in domestic trash [7]. It is estimated that over 90% of the water used worldwide is discharged without proper treatment [8]. Consequently, the removal and degradation of hazardous materials are attracting widespread attention in recent years. Organic pollutants are one of the most common hazardous species found in the environment. Some of them are common in people’s lives, such as pharmaceuticals and personal care products (PPCPs) and organic dyes [9, 10]. The use of PPCPs has increased in recent decades due to the growth of the world population, higher investments in the healthcare sector, and the aging of the population in industrialized countries [11]. PPCPs can be bioaccumulative, carcinogenic, and toxic to humans, wildlife, and flora, justifying the growing concern about their toxicity and disposal [12, 13]. It should also be emphasized that the COVID-19 pandemic has boosted the consumption of pharmaceuticals, which justifies investigating the remediation of these pollutants in water bodies [14]. The academic community has become very concerned about the increasing concentration of these products in urban sewage and the subsequent contamination of the environment [15]. Organic dyes are also pollutants of great concern nowadays. Several sectors use these materials, including the paper, food, textile, plastics, cosmetics, and paint industries [16]. More than 100000 different dyes are commercially available, and about 700000 tons of these materials are produced worldwide every year. From this amount, around 100 tons are disposed of as wastewaters each year due to the dyeing process [17]. When discharged in water bodies, the inherent intense coloration of such pollutants inhibits the transmission of sunlight into the water, adversely affecting the photosynthetic activity essential for water-dwelling organisms [18]. Besides, the biological oxidation of these pollutants consumes the oxygen dissolved in water, causing adverse health effects in humans and animals. They can also cause breathing difficulties, nausea, skin irritation, and cancer [19].

Several strategies have been used to remove organic pollutants from wastewater, including ozonation [20], adsorption, filtration [21], electrochemical oxidation [22, 23], and photocatalysis [24]. Among these methods, photocatalysis deserves to be highlighted because of its low energy consumption, high efficiency, and easy scalability. Titania (TiO\(_2\)) is a semiconductor photocatalyst that can be prepared as porous nanoparticles by combining the sol–gel process and hydrothermal treatment. Nonetheless, titania nanoparticles tend to form clusters in solution, which decreases the area available for adsorption and negatively affects their photocatalytic activity [25]. As a consequence, different materials have been used as a support to anchor/grow these nanoparticles and avoid their agglomeration. Hu et al. [26] reported a photocatalytic system for the removal of dye waste using cotton as a support material for TiO\(_2\). Gonçalves et al. [27, 28] loaded sol–gel-derived TiO\(_2\) nanoparticles on reduced graphene oxide nanosheets. In this work, metal–organic frameworks (MOFs) were used as support to grow TiO\(_2\) nanoparticles. MOFs are well known for their high specific surface area (SSA) and chemical versatility [29]. MOFs have been used in several photocatalytic applications, including H\(_2\) evolution, removal of organic pollutants from aqueous media, and CO\(_2\) reduction [30]. They have been doped with metals such as Pd and Pt to improve their photocatalytic activity [31]. Other strategies have also been employed to obtain visible light-active MOFs, including ligand functionalization, mixed-metal/linker, metal ions immobilization, ligands immobilization, and dye sensitization [32].
TiO2@MOF composites have already been used to remove organic dyes from liquid media. Different MILs (Materials Institute Lavoisier) matrices have been used for this purpose [33]. In the study of Hejazi et al. [34], MIL-100(Fe) was decorated with TiO2 and used to mineralize methylene blue (MB). Li et al. [35] investigated the photodegradation of the same pollutant by anchoring TiO2 nanoparticles on NH2-MIL-88B(Fe). TiO2@MIL-100(Cr) was employed to remove bisphenol A [36] and toluene [37]. Other MOFs such as HKUST-1 (The Hong Kong University of Science and Technology) have also been used to obtain heterostructures with TiO2, remove dyes [38] and synthesize ammonia [39]. However, few works available in the literature deal with the use of these matrices in the degradation/adsorption of NSAIDs [33], although these pollutants have attracted extensive attention in recent years. In this work, two different MOFs were used, namely aluminum trimesate (MIL-100(Al)) [40] and copper trimesate (HKUST-1) [41]. The preparation of MIL-100(Al) was recently described by Volkringer et al. [40]. However, this is the first time that the preparation of a TiO2@aluminum-based MOF composite is reported. MIL-100(Al) has higher thermal stability (up to 400 °C) and lower density when compared to other MIL-100(M) (M = Cr, Fe, Mn or V) matrices, which are strategic advantages [42]. Furthermore, Al deserves special attention since it is an inexpensive metal, which can be beneficial in several industrial applications [43]. Moreover, MIL-100(Al) has relatively large cages (up to 2.9 nm against 1.1 nm for HKUST-1), which may be a useful property during the adsorption of large molecules. On the other hand, HKUST-1 was chosen for comparative purposes because it is a commercially available MOF, which may be interesting when applying a post-synthetic modification approach. These materials were initially prepared by hydrothermal synthesis and then decorated with TiO2 nanoparticles following a sol–gel route [44]. The as-obtained samples were examined according to their structural properties and photocatalytic behavior. The TiO2-decorated MOFs were evaluated according to the photodegradation of organic pollutants (MB and NSAIDs—ibuprofen (IBP) and sodium diclofenac (DIC)) under near-ultraviolet (UV-A) light.

Materials and methods

Syntheses

MOF matrices

MIL-100(Al) was prepared as follows. Aluminum nitrate nonahydrate (Al(NO3)3·9H2O, Carlo Erba, 99%, 7.48 g), trimethyl-1-3-5-benzenetricarboxylate ((CH3COO)3-C6H3, Aldrich, 98%, 3.39 g), nitric acid solution (HNO3, Aldrich, 1 M, 25 mL), and deionized water (H2O, 91 mL) were initially poured in a 500-mL Teflon flask. The container was transferred to a stainless steel autoclave and placed in a furnace. It was subsequently heat-treated in air at 180 °C for 3 h at a heating rate around 2.6 °C min−1. Next, the autoclave was allowed to cool down to room temperature inside the furnace. A yellow solid was then recovered by centrifugation and stirred with 200 mL of anhydrous N,N-dimethylformamide (DMF, Aldrich, 99.8%) at 150 °C for 5 h. Next, the solid was collected by centrifugation, washed with absolute ethanol (EtOH, Aldrich), and air-calcined at 200 °C for 5 h. Around 2.3 g of a dried solid was collected after this step.

HKUST-1 was hydrothermally prepared as well. Copper(II) nitrate trihydrate (Cu(NO3)2·3H2O, Aldrich, 99%, 3.5 g), 1,3,5-benzene tricarboxylic acid ((COOH)3C6H3, Sigma-Aldrich, 98%, 2.1 g), EtOH (36 mL), and H2O (36 mL) were poured in a 500 mL Teflon container and then placed in a furnace. It was then heat-treated in air at 110 °C for 12 h using a heating rate of 1.4 °C min−1. After reaching room temperature, a dark blue solid was recovered by centrifugation, washed with EtOH, and calcined in air at 200 °C for 5 h. Around 2.5 g of a dried solid was collected after this step.

Sol–gel-derived TiO2

The growth of TiO2 nanoparticles on MIL-100(Al) and HKUST-1 followed a procedure similar to that reported by Hu et al. [44]. Briefly, 500 mg of the previously prepared MOF was dried under air at 150 °C for at least 5 h. Next, it was added under stirring to a solution containing 20 mL of titanium (IV) tetraisopropoxide (TTIP, Sigma-Aldrich 98%) and 26 mL of isopropyl alcohol (iPrOH, Aldrich 98%). The solution was sonicated for 30 min and kept under stirring for another 30 min. After 10 h, the
solid was recovered by centrifugation at 6000 rpm for 20 min and washed with IPrOH. It was subsequently aged for 48 h in air and then poured in a 350-mL Teflon container previously filled with 210 mL of deionized Milli-Q water. Next, the system was transferred to a stainless steel autoclave and heat-treated in air at 150 °C for 10 h. After cooling down to room temperature, a solid was recovered by centrifugation (20 min at 6000 rpm) and then air-dried at 80 °C for 72 h. The samples modified with titania were identified as TiO$_2$@MIL-100(Al) and TiO$_2$@HKUST.

For reference purposes, pure TiO$_2$ was also prepared following the procedure reported in a previous study [25]. A polymeric solution was initially prepared by mixing TTIP with a solution of H$_2$O, hydrochloric acid (HCl, Aldrich, 37%), and IPrOH. The loading of TTIP in this solution was 0.4 M, and the molar ratio of TIPT:H$_2$O:HCl was kept at 1:0.82:0.13. The solution was subsequently aged in air at room temperature for 72 h. Next, deionized water was added to MS to adjust the molar ratio of H$_2$O:TTIP to 90:1. The as-prepared solution was then autoclaved at 130 °C for 6 h. Finally, a nanocrystalline suspension was obtained by stirring the autoclaved solution at room temperature for 30 min to break particle agglomerates and sonication for 1 h to promote the redispersion of TiO$_2$ nanoparticles. The powdered material was subsequently obtained by drying at 70 °C for 48 h, followed by grinding in an agate mortar.

Characterizations

X-ray powder diffraction (PXRD) was conducted on a Philips-PANalytical diffractometer (PW1710) at a scan rate of 0.06° s$^{-1}$, using CuK$\alpha$ as the radiation source ($\lambda = 1.54$ Å). N$_2$ and Kr sorption were performed at the liquid nitrogen temperature (−196 °C) using a Micromeritics ASAP 2020 apparatus. The examined samples were previously degassed under vacuum at either 105 °C (HKUST-1) or 200 °C (MIL-100(Al)). The specific surface area (SSA) and pore size distribution of the examined samples were evaluated by the multipoint BET (Brunauer–Emmett–Teller) model and density functional theory (DFT) in the 0.02–0.3 $P/P_0$ range. Transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS) were conducted on an FEI microscope (Tecnai G2-20 SuperTwin) at an accelerating voltage of 200 kV. This microscope is equipped with a Si(Li) EDS detector (EDAX) with a 30 mm$^2$ window and a post-column Gatan Image Filter (GIF) Quantum SE System coupled with a bright and annular dark field (BF/ADF) STEM detector, Orius SC200 and GIF (US1000FTXP) CCD cameras. The samples used in these tests were previously dispersed in EtOH and sonicated at room temperature for 5 min. The obtained suspensions were dripped on carbon-coated grids. After drying in air at room temperature, those grids were used in TEM, EELS, EDS, and SAED examinations. Scanning electron microscopy (SEM) was conducted on a FEG microscope (Hitachi SU 5000) at an accelerating voltage of 5 kV, using samples previously sputter-coated with carbon. This microscope is equipped with a Si(Li) EDS detector (AZtec from Oxford Instruments) with a 60 mm$^2$ window. The apparent bandgap energy ($E_{\text{gap}}$) of the materials obtained in this study was evaluated by ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy at a resolution of 1 cm$^{-1}$ on a Shimadzu UV-2600 spectrometer. $E_{\text{gap}}$ was estimated by plotting the so-called Kubelka–Munk function [(F(R)hv)$^{1/2}$] as a function of the photon energy (hv), where $h$ is the Planck constant ($4.14 \times 10^{-15}$ eV s) and $v$ is the photon frequency (Hz). The index $n$ is dependent on the electron transition observed in the examined material, e.g., indirect allowed transition, direct allowed transition, indirect forbidden transition, or direct forbidden transition. As TiO$_2$ has an indirect bandgap, one considered $n = \frac{1}{2}$ in these calculations [45]. F(R) was assessed by Eq. (1), where $R$ is the reflectance (%) assessed by UV–Vis spectroscopy.

$$F(R) = \frac{(1 - R)^2}{2R}$$

(1)

The energy positions of the valence band ($E_{\text{VB}}$) and the conduction band ($E_{\text{CB}}$) edges were obtained by Eqs. (2) and (3) [46]. $E_c$ represents the energy of free electrons on the hydrogen scale (4.5 eV vs. SHE (standard hydrogen electrode)), and $X$ is the electronegativity of the semiconductor evaluated from the average between the electron affinity and the first ionization energy of an atom [47].

$$E_{\text{VB}} = X - E_c + 0.5E_g$$

(2)

$$E_{\text{CB}} = E_{\text{VB}} - E_g$$

(3)
Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Alpha spectrometer using an attenuated total reflectance (ATR) accessory and a diamond crystal as the reflective element. The spectra were taken at a resolution of 4 cm\(^{-1}\) and 128 scans. Raman spectroscopy was carried out on a LabRaman HR-Evolution (Horiba Scientific) micro-spectrometer equipped with 600 lines per mm grating and an Olympus objective, using a 515-nm laser as the excitation source. Thermogravimetry (TG) was carried out on a TGA 92 Setaram thermoanalyzer in air at 5 °C min\(^{-1}\). DTG (differential thermogravimetry) profiles were obtained by calculating the first derivative of the collected thermograms. Spin trapping electron paramagnetic resonance (EPR) was carried out at room temperature on an X-band (\(\approx 9.4\) GHz) Magnetech MiniScope MS400 spectrometer. This technique allows examining short-lived free radicals, particularly reactive oxygen species (ROS). The experimental parameters used in these tests were: microwave power = 10 mW, modulation field = 100 kHz, modulation amplitude = 0.2 mT, center field = 337 mT, scan time = 60 s, and number of integration points = 4096. Aqueous solutions of IBP (10 mg L\(^{-1}\)) and the examined photocatalyst (200 mg L\(^{-1}\)) were initially prepared at room temperature. Solutions containing either N-tert-butyl-\(\alpha\)-phenylnitrone (PBN, TCI America, Japan, 98%) or 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Oakwood, USA, 96%) were used as spin traps in these tests. The loading of PBN and DMPO in these solutions was kept at about 200 and 10 mg L\(^{-1}\), respectively. Blank experiments were also conducted in the absence of a photocatalyst aiming to evaluate the stability of the studied pollutants under UV-A light. It was observed that these organic compounds do not degrade under UV-A light to such an extent that their stability of the studied pollutants under UV-A light. Photocatalytic tests

The samples’ photoactivity was evaluated in terms of the photodegradation of MB (Synth, Brazil), IBP (Florien Pharmaceutical Supplies, Brazil), and DIC (Henan Dongtai Pharmacy Limited Company, China). These materials were initially dissolved in distilled water at room temperature under stirring. The concentrations of the drugs and photocatalysts in the as-prepared solution were 10 and 200 mg L\(^{-1}\), respectively. The initial pH of this solution was about 8. Then, the solution was poured into a photoreactor containing an Osram Dulux 9 W/78 UV-A lamp (1.5 W between 315 and 400 nm). The solution temperature was kept constant at 25 °C using a cooling system coupled to the reactor. The solution was initially kept under stirring at room temperature in the dark overnight for adsorption purposes. Next, the UV-A lamp was turned on, and aliquots of the solution were taken as a function of time and used to monitor the drug’s concentration. The aliquots were initially centrifuged at 6000 rpm for 5 min to avoid interference from suspended particles. The particle-free supernatant was then transferred to quartz cuvettes and examined by UV–Vis spectroscopy. The light absorption at 222 nm, 276 nm, and 665 nm was used as a reference for IBP, DIC, and MB, respectively. Blank experiments were also conducted in the absence of a photocatalyst aiming to evaluate the stability of the studied pollutants under UV-A light. It was observed that these organic compounds do not degrade under UV-A light to such an extent that their photolysis can be neglected.

The kinetic model of Langmuir–Hinshelwood (L–H) was employed to evaluate the photoactivity of the examined materials. This model is expressed by Eq. (4), where \(r\) is the pollutant oxidation rate (mg L\(^{-1}\) h\(^{-1}\)), \(C\) the pollutant concentration (mg L\(^{-1}\)), \(t\) the illumination time (h\(^{-1}\)), and \(K\) the adsorption coefficient (L mg\(^{-1}\)). For highly diluted solutions, e.g., \(C_0\) in the millimolar range, Eq. (4) can be rewritten as expressed in Eq. (5), where \(k_\text{app} (h^{-1})\) is the apparent first-order rate constant. The
constant \( k_{\text{app}} \) can be evaluated by plotting \( \ln(C/C_0) \) as a function of time.

\[
 r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (4)
\]

\[
 \ln\left(\frac{C}{C_0}\right) = kKt = k_{\text{app}}t \quad (5)
\]

Results

Figure 1 shows the XRD patterns obtained in this work. The diffraction lines observed at 2\( \theta \) around 3.6\(^\circ\), 4.2\(^\circ\), 5.1\(^\circ\), 6.1\(^\circ\), and 6.5\(^\circ\) have been associated with the (220), (311), (400), (442), and (333) crystal planes of MIL-100(Al) \[40, 48\]. Additional diffraction lines at 2\( \theta \) = 25.5\(^\circ\), 38.2\(^\circ\), 48.1\(^\circ\), and 54.4\(^\circ\) were observed after the growth of TiO\(_2\) on this MOF. These diffraction lines have been attributed to the (101), (004), (220), and (211) crystal planes of anatase \[28\]. The main diffraction lines of HKUST-1 were observed at 2\( \theta \) around 6.9\(^\circ\), 9.5\(^\circ\), 11.7\(^\circ\), 19.1\(^\circ\), and 26.1\(^\circ\), which are attributed to the (200), (220), (222), (440), and (731) crystal planes \[49\]. The formation of TiO\(_2\) on it caused its main peaks at 9.5\(^\circ\) and 11.7\(^\circ\) to disappear, while a strong diffraction line at 2\( \theta \) = 27.5\(^\circ\) was observed. This diffraction line has been associated with the (110) crystal plane of rutile \[25\]. The pure TiO\(_2\) sample showed anatase as the main crystalline phase (XRD pattern not shown here), which is in line with previous studies \[25, 27, 28\].

Figure 2 displays the FTIR spectra taken for MIL-100(Al), TiO\(_2\)@MIL-100(Al), HKUST-1, and TiO\(_2\)@HKUST. The inset exhibited in Fig. 2 shows a spectrum collected for a pure TiO\(_2\) sample. The spectra obtained for MIL-100(Al) and HKUST-1 are analogous to those reported elsewhere \[50–52\]. Additional absorption bands are noticed when the spectra of

![Figure 1](image-url)  
*Anatase  
□Rutile  
**TiO\(_2\)@MIL-100(Al)  
MIL-100(Al)  
**TiO\(_2\)@HKUST  
HKUST-1  
Anatase: 21-1272  
Rutile: 86-0147  
JCPDS cards  

Figure 1 XRD patterns of the samples obtained in this work. The JCPDS file numbers 21-1272 and 86-0147 were used as the references for anatase and rutile, respectively. These JCPDS cards are also exhibited for reference purposes.
TiO$_2$-loaded samples are compared to those collected for the pure MOFs. The bands observed from 400 to about 920 cm$^{-1}$ have been assigned to Ti–O bonds [53, 54]. The features at 1390 cm$^{-1}$ and 1490 cm$^{-1}$ are associated with the bending mode of CH$_3$ and CH$_2$ groups [55]. These bands can be related to IPrOH, EtOH, or DMF used to prepare the MOF matrices and TiO$_2$ nanoparticles. It can be observed that the absorption bands ascribed to Ti–O bonds are so strong in TiO$_2$@MIL-100(Al) that the bands associated with MIL-100(Al) from 400 to 770 cm$^{-1}$ are not noticeable in the composite; the superposition of the absorption bands related to TiO$_2$ and MIL-100(Al) does not allow the latter signals to be identified in the composite’s spectrum. The same behavior is not observed for TiO$_2$@HKUST, where the absorption bands of HKUST-1 between 400 and 825 cm$^{-1}$ observed in the spectra of HKUST-1 and TiO$_2$@HKUST are, respectively, related to Cu–Cu stretching [60, 61] and C–H bending of 1,3,5-benzentricarboxylate (BTC) [62]. Bands assigned to rutile were identified in the spectrum of TiO$_2$@HKUST, which is also in line with XRD (Fig. 1). The bands at about 225 cm$^{-1}$, 425 cm$^{-1}$, and 600 cm$^{-1}$ have been related to the second-order scattering (SOS), $E_g$, and $A_{1g}$ modes of rutile [63].

The value of $E_{\text{gap}}$ assessed for MIL-100(Al) and TiO$_2$@MIL-100(Al) were, respectively, 3.70 eV and 3.27 eV, revealing that the growth of TiO$_2$ on MIL-100(Al) changed its electronic structure and decreased its bandgap. On the other hand, no noticeable change in this value was observed between HKUST-1 and TiO$_2$@HKUST since $E_{\text{gap}}$ remained around 3.32 eV. Anatase and rutile have $E_{\text{gap}}$ around 3.2 eV and 3.0 eV, respectively [64]. The pure TiO$_2$ displayed an $E_{\text{gap}}$ around 3.2 eV, which...
was expected since anatase is its main phase (Fig. 1). Figure 4 displays the TG and DTG profiles obtained in this study. The profiles obtained for the pure MOF matrices are similar to those already reported in the literature [65, 66]. The mass loss at temperatures up to 100 °C is ascribed to the removal of water and other physisorbed molecules [41]. The mass loss between 100 and 200 °C in HKUST-1 is ascribed to the removal of coordinated water [67]. The sharp decrease in weight observed at about 300 °C and 460 °C for HKUST-1 and MIL-100(Al) has been associated with the elimination of organic linkers [41, 68, 69]. A distinct thermal behavior is noticed when the TiO2-containing samples are compared to the pure MOFs, as the former had a smaller mass loss than the latter. This difference could be related to the presence of TiO2 in the composites, which displays high thermal stability in the examined temperature range [34]. One observes that the difference in mass loss detected for the pure MOF and the corresponding TiO2-loaded composite is higher for MIL-100(Al) (about 44%) than for HKUST-1 (about 7%). Such a difference could be associated with the distinct TiO2 loadings in these MOFs.

Figure 5 depicts SEM, TEM, EELS, and SAED results obtained in this work. Particles with sharp edges are observed for MIL-100(Al), which agrees with the literature [70, 71]. As was expected, the EELS spectrum of this material indicated the presence of carbon, oxygen, and aluminum in MIL-100(Al). A distinct structure was noticed for TiO2@MIL-100(Al), where TiO2 nanoparticles as small as 5 nm were observed anchored to MIL-100(Al). SAED analyses revealed that the titania nanoparticles observed in TiO2@MIL-100(Al) are related to anatase; it is possible observing the main Debye–Scherrer concentric rings of anatase in the SAED pattern displayed in Fig. 5a. This result is in line with XRD (Fig. 1) and reveals that anatase is the main polymorph of titania in TiO2@MIL-100(Al). The EELS spectrum collected for a titania nanoparticle is also exhibited in Fig. 5a. The molar composition (mol.%) of this particle was evaluated to be 34Ti–66O, which gives an atomic ratio of 2O:1Ti, as it was expected for TiO2.

Octahedron-shaped particles were observed in the SEM micrographs of HKUST-1 (Fig. 5b), which agrees with other works [72]. However, the same structure was not observed in the TEM micrographs displayed in Fig. 5b, suggesting that HKUST-1 has
collapsed during its preparation for TEM (sonication in EtOH at room temperature for 5 min). This behavior is due to the low chemical stability of HKUST-1 under moist conditions at room temperature [67]. The EELS spectrum collected for this sample revealed the presence of carbon, oxygen, and copper. Needle-shaped crystals attributed to Cu$_2$(BTC)(OH)(H$_2$O) [61, 67] are noticed in the TEM micrographs. Moreover, TiO$_2$ nanoparticles of about 6 nm in size were observed anchored on these crystals. The EELS spectrum obtained for a titania nanoparticle is exhibited in Fig. 5b. The molar composition (mol.%) evaluated for this nanoparticle was also 34Ti – 66O, as was expected. A concentric Debye–Scherrer ring ascribed to the (110) crystal plane of rutile was observed in the obtained SAED pattern (Fig. 5b), reinforcing that TiO$_2$ has crystalized as rutile on HKUST-1.

Figure 6 shows the gas sorption isotherms collected here and the pore size distributions evaluated using the NLDFT model. N$_2$ was used to analyze MIL-100(Al), TiO$_2$@MIL-100(Al), and HKUST-1, while TiO$_2$@HKUST was examined with Kr; the porosity of TiO$_2$@HKUST was so low that it was not possible to exam it with N$_2$, which is why Kr was used. Both MIL-100(Al) and HKUST-1 displayed a type I isotherm, typically observed in microporous solids [73]. The growth of TiO$_2$ on these matrices dramatically changed their isotherms; TiO$_2$@MIL-100(Al) showed a type IV isotherm commonly attributed to mesoporous materials, while TiO$_2$@HKUST showed a much lower porosity. These changes in the pore structure are also noticed in terms of SSA. MIL-100(Al) showed an SSA of 1787 m$^2$ g$^{-1}$, but this value lowered to 417 m$^2$ g$^{-1}$ after growing TiO$_2$ on it. HKUST-1 experienced a change in SSA from 1360 to 8 m$^2$ g$^{-1}$ after its chemical modification.

Figure 7 displays spin trapping EPR spectra obtained with DMPO and using aqueous solutions containing TiO$_2$@MIL-100(Al) (Fig. 7a) or TiO$_2$@HKUST (Fig. 7b). While the dark spectrum of TiO$_2$@MIL-100(Al) does not present any paramagnetic species, signals due to different spin adducts are observed after 10 min of UV-A illumination. On the other hand, the EPR spectrum of TiO$_2$@HKUST shows different spin adducts even in the dark that are transformed after 10 min of UV-A illumination. The
presence of spin adducts before the UV-A illumination of TiO2@HKUST indicates that ROS were present even before adding the spin trap. In contrast to TiO2@MIL-100(Al), TiO2@KHUST does not induce ROS formation under UV-A light.

Figure 8a exhibits the spin trap EPR spectra taken for TiO2@MIL-100(Al) in the presence of PBN in an EtOH-H2O solution (1:1). PBN was used as a spin trap in this work because of the high stability of its spin adducts, which allows evaluating the kinetics of radical generation. The EPR spectrum collected during the UV-A illumination of TiO2@MIL-100(Al) is associated with the capture of an \( \alpha \)-hydroxyethyl radical (H3C–CH–OH) by PBN (Fig. 8b). This signal arises from six spin transitions and is due to the hyperfine interaction of an unpaired electron centered on an oxygen atom with the nuclear spin \( I = 1 \). Moreover, the nuclear spin \( I = \frac{1}{2} \) of \(^1\text{H} \) at a \( \beta \)-site of PBN could also contribute to this signal. The values of the isotropic hyperfine interaction constants obtained by spectrum simulation (Fig. 8b) were \( a_{\text{N}} = 1.48 \text{ mT} \) and \( a_{\text{H}}(\beta) = 0.30 \text{ mT} \). They are consistent with those already reported elsewhere [74]. The \( \alpha \)-hydroxyethyl radical results from the interaction between hydroxyl radicals and ethanol molecules.

The use of PBN as a spin trap confirmed the generation of \( \alpha \)-hydroxyethyl radicals, which, similar to the DMPO spin trapping experiment conducted with TiO2@MIL-100(Al), evidenced its ability to exchange charge carriers with the solvent molecules under illumination with UV-A light. The same spin trapping experiments were also conducted with TiO2@HKUST. However, no PBN spin adducts were generated with this catalyst under UV-A light.

The evaluation of the concentration of spin adducts generated upon the capture of \( \alpha \)-hydroxyethyl by
PBN during UV-A illumination was performed from double integration of the EPR signals (Fig. 8a). Next, this result was compared with the signal intensity of a sample of known concentration (4-hydroxy-tempo, Figure 6). Gas sorption isotherms and pore size distributions of the samples prepared in this work. MIL-100(Al), TiO$_2$@MIL-100(Al), and HKUST-1 were examined using N$_2$, while TiO$_2$@HKUST was analyzed with Kr.

Figure 6  Gas sorption isotherms and pore size distributions of the samples prepared in this work. MIL-100(Al), TiO$_2$@MIL-100(Al), and HKUST-1 were examined using N$_2$, while TiO$_2$@HKUST was analyzed with Kr.

Figure 7  EPR spin trapping experiments conducted with DMPO in an aqueous solution containing either a TiO$_2$@MIL-100(Al) or b TiO$_2$@HKUST. The experimental EPR spectra were obtained in the dark and after 10 min of UV-A illumination. Simulated EPR spectra for the DMPO spin adducts: DMPO* ($\delta_N = 1.46$ mT), DMPO/ OH ($\delta_N = \delta_{H(\beta)} = 1.50$ mT), and DMPO/ H ($\delta_N = 1.56$ mT and $\delta_{H(\beta)} = 2.39$ mT). The reader is encouraged to see this figure in color in the online version of this work.
TEMPOL, 1 mM). The kinetics of spin adducts generation for the two samples are displayed in Fig. 8c. The uncertainty in the spin adduct concentration is assumed to be within 10% of the value obtained by integration. The linear function associated with the kinetics of spin adducts generation for TiO2@MIL-100(Al) is characteristic of a first-order regime. This behavior reveals that the formation of OH radicals by charge carriers exchange is a primary process and is not a secondary process resulting from cross reactions. The generation kinetics of spin adduct (PBN/H3C–/C1CH–OH) exhibited in Fig. 8c establishes the photocatalytic activity of TiO2@MIL-100(Al) under illumination with UV-A light. However, this characteristic was negligible on TiO2@HKUST.

Figure 9 displays the spin trapping EPR results obtained using a DMPO–acetonitrile solution. As mentioned before, these tests were conducted to evaluate the formation of superoxide radicals under UV-A light. The most intense EPR lines occurred for a UV-A illumination time of 15 min for TiO2@MIL-100(Al) (black line) and TiO2@HKUST (green line). From EPR spectrum simulations (red line), two different DMPO adducts were identified: (i) DMPO* (dark yellow), which is a spin adduct associated with
the degradation of DMPO resulting from protonation of the spin trap molecule, and (ii) DMPO/*OO\(^-\) (blue), which is formed after the capture of superoxide radicals. The associated spin Hamiltonian parameters are \(a_N = 1.31\) mT, \(a_{H(b)} = 1.06\) mT, and \(a_N = 1.39\) mT for DMPO/*OO\(^-\) and DMPO\(^*\), respectively \[75\]. The sum of both calculated EPR spectra is shown in red, which corresponds to the EPR spectrum of TiO\(_2@\)MIL-100(Al). For TiO\(_2@\)HKUST, the major adduct is that related to DMPO\(^*\), which is also observed just after the solution preparation without illumination. These results confirm that the TiO\(_2@\)MIL-100(Al) catalyst produces both hydroxyl and superoxide radicals under UV-A illumination, forming both electrons and holes that produce superoxide and hydroxyl radicals by interaction with the dissolved molecular oxygen and solvent molecules.

Figure 10a–c exhibits the photocatalytic tests conducted using MB, DIC, or IBP. The photocatalytic behavior evaluated for a pure TiO\(_2\) sample is shown in Fig. 10a for reference purposes. In the tests conducted using MB as the pollutant, pure TiO\(_2\) showed slightly higher photoactivity than TiO\(_2@\)HKUST, but lower photoactivity than TiO\(_2@\)MIL-100(Al). One observes that the growth of TiO\(_2\) nanoparticles on MIL-100(Al) and HKUST-1 positively affected their photocatalytic performance. The values of \(k_{app}\) assessed using Eq. (5) are summarized in Table 1. It can be observed that TiO\(_2@\)MIL-100(Al) was the best performing sample, but the formation of TiO\(_2\) nanoparticles on HKUST-1 also improved its photocatalytic behavior. Figure 11 depicts the electronic structures suggested for TiO\(_2@\)MIL-100(Al) and TiO\(_2@\)HKUST.

**Discussion**

The chemical modification of MIL-100(Al) by a hydrothermal sol–gel route led to the growth of anatase nanoparticles on it. This behavior was observed by XRD (Fig. 1), FTIR (Fig. 2a), Raman (Fig. 3a), and SAED (Fig. 5a). TEM tests revealed that these nanoparticles are as small as 5 nm (Fig. 5a). TG pointed out that the difference between the mass loss detected for the pure MOF and the respective TiO\(_2\)-containing composite was more significant for MIL-100(Al) than for HKUST-1 (Fig. 4). A mass balance was carried out to evaluate the loading of TiO\(_2\) in the prepared composites. This calculation was based on

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**Figure 10** Photocatalytic tests performed using a MB, b DIC, and c IBP as the pollutants. The solid lines connecting the data points are only a guide to the eyes.
Eq. (6), where \( M_D \) represents the mass of the dried material (g), \( M_L \) is the mass of organic linkers in the MOF matrix (g), and \( M_C \) is the mass of the calcined material (g). The values of \( M_D \), \( M_L \), and \( M_C \) were estimated considering the mass loss steps observed at about 400 °C, 600 °C, and 800 °C, respectively. It should be expected that after calcination, the remaining mass in the composites is partially due to \( \text{TiO}_2 \) and partly due to residues present in the MOF. This behavior is shown in Eq. (7), where \( M_{\text{MOF}} \) and \( M_{\text{TiO}_2} \) are the masses of the MOF matrix and \( \text{TiO}_2 \) nanoparticles in the composites at 800 °C. The ratio between the masses of dried and calcined MOFs is related to their contribution to the final mass of the calcined composites, as shown in Eq. (8). This estimation revealed that the titania loading in \( \text{TiO}_2@\text{MIL-100(Al)} \) and \( \text{TiO}_2@\text{HKUST} \) was about 68 wt.% and 9 wt.% respectively. This result supports that \( \text{TiO}_2 \) has been incorporated into a significant amount in MIL-100(Al), while its loading in HKUST-1 is comparatively low. Indeed, the superposition of the FTIR absorption bands ascribed to anatase and MIL-100(Al) in \( \text{TiO}_2@\text{MIL-100(Al)} \) did not allow the MOF-related bands to be observed (Fig. 2a). This behavior is due to the high concentration of \( \text{TiO}_2 \) in MIL-100(Al), which agrees with TG/DTG.

\[
M_D = M_L + M_C
\]

\[
M_{\text{Composite}} = M_{\text{MOF}} + M_{\text{TiO}_2}
\]

\[
M_{\text{Composite}} = M_{\text{MOF}} \times \frac{M_{\text{C,MOF}}}{M_{\text{D,MOF}}} + M_{\text{TiO}_2}
\]

The formation of anatase nanoparticles on MIL-100(Al) was accompanied by a decrease in its SSA from 1787 to 417 m² g⁻¹, as well as a change in the shape of its adsorption isotherm (Fig. 6). The pore size distribution of MIL-100(Al) was also affected after the grown of \( \text{TiO}_2 \) nanoparticles on it, shifting this curve toward larger pores. Incorporating \( \text{TiO}_2 \) into MIL-100(Al) gave rise to pores between 4 and

| Pollutant | Sample       | \( k_{\text{app}} \) (h⁻¹) |
|----------|--------------|-----------------------------|
| MB       | TiO₂         | 0.50                        |
|          | MIL-100(Al)  | 0.12                        |
|          | TiO₂@MIL-100 | 1.29                        |
|          | HKUST-1      | 0.05                        |
|          | TiO₂@HKUST   | 0.29                        |
| DIC      | MIL-100(Al)  | 0.07                        |
|          | TiO₂@MIL-100 | 0.21                        |
|          | HKUST-1      | ~                            |
|          | TiO₂@HKUST   | 0.03                        |
| IBP      | MIL-100(Al)  | 0.08                        |
|          | TiO₂@MIL-100 | 0.37                        |
|          | HKUST-1      | 0.01                        |
|          | TiO₂@HKUST   | 0.02                        |

The values not shown in this table were negligible and were intentionally omitted.
10 nm. In comparison, pores with sizes around 1.7 nm disappeared in MIL-100(Al) after this chemical modification. This SSA reduction and the modification of the MOF pore structure suggests a partial blockage of its cages by TiO2 nanoparticles. Also, some of them may have collapsed during the growth of these nanoparticles. It is worth mentioning that the sol–gel method used in this study gives rise to mesoporous TiO2 samples with SSA of about 170 m² g⁻¹ [28].

The chemical modification of HKUST-1 caused the formation of rutile on it, which is supported by XRD (Fig. 1), Raman (Fig. 3b), and SAED (Fig. 5b). The rutile particles formed on HKUST are as small as 6 nm. It also appears that the crystalline structure of this MOF partially collapsed during the sol–gel process, which is evidenced by the disappearance of its main diffraction lines at 2θ about 9.5 and 11.7° [76]. This behavior could justify the low porosity evaluated for TiO2@HKUST; the value of SSA assessed for HKUST-1 decreased from 1360 to 8 m² g⁻¹ after the incorporation of TiO2. As mentioned before, the porosity of TiO2@HKUST was so low that it was not possible to evaluate its SSA with N2, which is why Kr was used (Fig. 6). It was also observed the appearance of diffraction lines at 2θ around 9.0° and 10.0° after the growth of TiO2 nanoparticles on HKUST-1. These lines are due to the formation of Cu2(BTC)(OH)(H₂O), which has been ascribed to the replacement of CuO₄(H₂O) copper centers in HKUST for long chains composed of CuO₃(OH)₂ and CuO₄(OH)(H₂O) units, as expressed in Eq. (9) [67].

\[
2\text{CuO}_4(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{Cu}_3\text{O}_5(\text{OH})_2 + \text{CuO}_4(\text{OH})(\text{H}_2\text{O})^- + \text{H}^+ \quad (9)
\]

The sol–gel route used here usually gives rise to anatase nanoparticles [27, 28]. Although the formation of rutile on HKUST-1 could be unexpected, it may be ascribed to the acidification of the solution during the transformation of Cu₃(BTC)₂ into Cu₂(BTC)(OH)(H₂O), as evidenced in Eq. (9). This behavior could favor the rutile formation due to the low concentration of OH⁻ ligands in Ti(IV) complexes, allowing corner-shared bonds to give rise to a TiO₂ lattice [77]. As discussed before, the TiO₂ loading in TiO2@HKUST was evaluated to be about 9 wt.% (Fig. 4b and Eqs. (6) to (8)). The smaller concentration of TiO₂ in TiO2@HKUST compared to TiO2@MIL-100(Al) was also evidenced by FTIR (Fig. 2).

Before evaluating the NSAIDs, photocatalytic tests were initially conducted using MB as a model pollutant (Fig. 10a). This compound was chosen because it is relatively inexpensive, easily accessible, and has low toxicity. HKUST-1 and MIL-100(Al) showed photocatalytic activities of 0.05 h⁻¹ and 0.12 h⁻¹, respectively. They removed 18% and 35% of MB after 4 h of irradiation with UV-A light. The growth of TiO₂ nanoparticles on these matrices led to composites with k_app of 0.29 h⁻¹ (TiO2@HKUST) and 1.29 h⁻¹ (TiO2@MIL-100(Al)). The former removed 68% of MB and the latter 90%. Thus, it is clear that the chemical modification of HKUST-1 and MIL-100(Al) with TiO₂ positively affected their photoactivity. The photocatalytic performance of pure TiO₂ was higher than that exhibited by TiO2@HKUST, but lower than that displayed by TiO2@MIL-100(Al), removing 70% of the dye at the same conditions. It is worth mentioning that the photolysis of MB was negligible (below 1%). Such behavior may be related to the loading of TiO₂ in these materials: 9 wt.% for TiO2@HKUST and 68 wt.% for TiO2@MIL-100(Al). The collapse of HKUST-1 and the consequent formation of a low-porosity structure during the sol–gel step may be responsible for the low concentration of TiO₂ on it, which gave rise to fewer sites for the heterogeneous nucleation of titania nanoparticles when compared to MIL-100(Al). It is also worth stressing that anatase and rutile were the polymorphs of titania observed on MIL-100(Al) and HKUST-1. It is well established that anatase has a higher photocatalytic activity than rutile due to its larger SSA, smaller particle size, and higher adsorption capacity [78]. Moreover, the photogenerated charge carriers (electrons and holes) have lower mobility in anatase, which mitigates their recombination and improves anatase photoactivity [79].

The growth of TiO₂ on MOFs also increased their photocatalytic activity in tests performed using NSAIDs, i.e., DIC and IBP. However, this effect was more pronounced for MIL-100(Al); while MIL-100(Al) removed 12% of DIC and 7% of IBP after 240 min of UV-A illumination (k_app = 0.07 h⁻¹ and 0.08 h⁻¹), TiO2@MIL-100(Al) was able to remove 55% of DIC and 62% of IBP (k_app = 0.21 h⁻¹ and 0.37 h⁻¹). This behavior can be related to the high concentration of TiO₂ on this sample (about 62 wt.%). Moreover, a decrease of E_gap from 3.70 to 3.27 eV was observed after the growth of TiO₂ on MIL-100(Al), which may also contribute to the improved photocatalytic
behavior of the composite due to a more effective formation of charge carriers during UV-A illumination. Although the growth of TiO\textsubscript{2} on HKUST-1 had a minor effect on its photocactivity, the presence of rutile on it also enhanced its performance; while HKUST-1 had a negligible capacity to photodegrade DIC and IBP, TiO\textsubscript{2}@HKUST has removed 8\% of DIC and 7\% of IBP (k\textsubscript{app} = 0.03 h\textsuperscript{-1} and 0.02 h\textsuperscript{-1}) under UV-A light. The photolysis of DIC and IBP were insignificant (< 1\%) and are not displayed here.

The higher ability of the tested samples to photodegrade MB compared to DIC or IBP can be related to the pKa values of these pollutants. While MB has a pKa below 1.0 [80], DIP and IBP have pKa around 4.0 [81] and 5.2 [82]. The Henderson–Hasselbalch equation [83] establishes a relationship between pH and pKa as demonstrated in Eq. (10), where [A\textsuperscript{-}] and [HA] are the concentrations of the deprotonated and protonated forms of an acidic species.

\[
pH = pKa + \log \frac{[A^-]}{[HA]} \tag{10}
\]

According to Eq. (10), at pH above pKa, a significant number of the pollutant’s functional groups are protonated, revealing that it has a positively charged surface. The pH of the catalyst-containing solutions stabilized at about 6.0 after some time. This finding reveals that MB was highly charged during the photocatalytic tests, while DIP and IBP had few protonated groups. Such a scenario could favor the adsorption of MB molecules on the catalysts’ surface. In contrast, the electrostatic interaction between the pollutants and catalysts was impaired for DIC and IBP, negatively affecting their photodegradation. The photodegradation of DIC and IBP could be improved by changing the pH of the photocatalyst-containing solution. Nonetheless, this approach is beyond the scope of this work.

Spin trap EPR tests were performed to investigate the generation of radicals responsible for the photodegradation of organic pollutants. Two spin adducts were observed after UV-A illumination and identified using the Easyspin\textsuperscript{®} simulation software [84]. The EPR signal of the first spin adduct (blue line in Fig. 7) is characterized by a hyperfine interaction between an unpaired electron (S = ½), arising from a nitroxide group with the nuclear spin (I = 1) of \textsuperscript{14}N (99.6\%). This unpaired electron also interacts with the nuclear spin (I = ½) of the hydrogen atom (\textsuperscript{1}H) at a β-site of DMPO, giving rise to six possible electronic spin transitions. The values of the isotropic hyperfine interaction constants obtained after simulating this spectrum were \(a_N = a_I(\text{H}) = 1.50\) mT, which agrees with the values already reported for the DMPO/OH adduct [85, 86]. The spin adduct identified as DMPO\textsuperscript{+} (magenta lines in Fig. 7) is not associated with the capture of any specific ROS, but with the deprotonation of DMPO, resulting in a hyperfine interaction triplet between the electronic spin and the nuclear spin I = 1 of \textsuperscript{14}N (a\textsubscript{N} = 1.46 mT) [87]. This signal can be related to the interaction of the UV-A light with DMPO molecules. The formation of hydroxyl radicals (OH) during the UV-A illumination of TiO\textsubscript{2}@MIL-100(Al) indicates the production of ROS derived from the exchange of charge carriers between the catalyst and solvent (type I mechanism). Another ROS probably formed during the illumination of the suspended catalyst particles is the superoxide radical (O\textsubscript{2}\textsuperscript{-}), which is associated with excited electrons in the catalyst particles and molecular oxygen dissolved in the solvent. The absence of spin adducts associated with the capture of O\textsubscript{2}\textsuperscript{-} radicals is probably due to their short half-life of a few seconds and their lower concentration. The DMPO/OH spin adduct may be due to a direct formation process involving hydroxyl radicals or a secondary formation process involving superoxide radicals [88]. This may be another reason for the composites to degrade more MB than IBP and DIC; OH radicals are the main species derived from the degradation of MB, whereas in O\textsubscript{2}\textsuperscript{-} radicals play a key role an important role in the degradation of NSAIDs [34, 89].

A schematic representation of the heterojunctions formed between TiO\textsubscript{2} and the MOFs studied here is displayed in Fig. 11. \(E_{VB}\) and \(E_{CB}\) were obtained using Eqs. (2) and (3), which provide valuable information about the mechanism and the type of heterostructure formed by these two solids. In this case, TiO\textsubscript{2}@MIL-100(Al) was found to present a type I heterostructure, whereas TiO\textsubscript{2}@HKUST-1 has a type II heterojunction. Thus, in TiO\textsubscript{2}@MIL-100(Al) both the reduction and oxidation processes occur on TiO\textsubscript{2}. On the other hand, for TiO\textsubscript{2}@HKUST-1 oxidation takes place in the MOF matrix, while reduction occurs on TiO\textsubscript{2}.

Table 2 compares this study with others already published. It is worth mentioning that this is the first time that an aluminum-based MOF–TiO\textsubscript{2} heterojunction has been used in the photocatalysis of IBP and DIC. One observes from Table 2 that the


| Pollutant | MOF     | Titanium precursor | TiO₂ loading (wt.%) | Radiation source | Catalyst concentration (mg L⁻¹) | Pollutant concentration (mg L⁻¹) | Removal efficiency (%) | Sample designation | SSA (m² g⁻¹) | References |
|-----------|---------|--------------------|---------------------|------------------|-------------------------------|-------------------------------|------------------------|-------------------|-------------|------------|
| MB        | MIL-100(Fe) | TTIP   | ND                  | 400 W Hg         | 600                          | 40                             | 54.7 (without H₂O₂)  | TM/5             | 120         | [34]       |
|           | 88B(Fe)   | NH₂-MIL-TBT      | 13.7                | 5 W LED          | 200                          | 100                            | < 40 (without H₂O₂)  | SU-3             | ND*         | [35]       |
|           | HKUST-1   | TiO₂    | ND                  | 300 W Xe         | 500                          | 20                             | 91                     | 0.02TiO₂@HKUST-1   | 982         | [38]       |
|           | HKUST-1   | TTIP   | ND                  | Hg–Xe            | 3000                         | 127                            | ND                     | TiO₂@Cu₂BTC₂       | 120         | [90]       |
|           | HKUST-1   | TTIP   | ND                  | UV-A             | 200                          | 31.6                           | 82.6                   | CuFe₂O₄/TiO₂/CuBTC | ND         | [91]       |
|           | MIL-101(Cr) | TBT    | 13.8                | UV-A             | 1000                         | 20                             | > 99                   | TiO₂-MIL-101       | 531         | [92]       |
|           | MIL-100(Al) | TTIP  | 68                  | 9 W/78 UV-A      | 200                          | 10                             | 90                     | TiO₂@MIL-100(Al)   | 417         | This work  |
| DIC       | MIL-100(Al) | TTIP  | 68                  | 9 W/78 UV-A      | 200                          | 10                             | 55                     | TiO₂@MIL-100(Al)   | 417         | This work  |
| IBP       | MIL-100(Al) | TTIP  | 68                  | 9 W/78 UV-A      | 200                          | 10                             | 62                     | TiO₂@MIL-100(Al)   | 417         | This work  |

*TBT* titanium(IV) butoxide, *ND* not defined
TiO$_2$@MIL-100(Al) composite prepared here displayed a higher removal efficiency than many previously published works, which reinforces its promising use in photocatalytic processes. TiO$_2$@HKUST has a much lower photoactivity than TiO$_2$@MIL-100(Al), which is related to its non-porous structure and, consequently, to a lower concentration of titania nanoparticles on it. Moreover, it was observed that titania is present as rutile in TiO$_2$@HKUST, which has a lower photocatalytic activity than anatase (main crystalline phase of titania in TiO$_2$@MIL-100(Al)). These properties justify the lower photocatalytic activity of TiO$_2$@HKUST when compared to TiO$_2$@MIL-100(Al). The collapse of HKUST-1 could be inhibited by changing the sol–gel processing of TiO$_2$; for instance, the hydrothermal temperature and time could be changed, in addition to the molar composition of the starting sol. In a further step, it is intended to promote the chemical etching of TiO$_2$@MIL-100(Al), aiming to remove MIL-100(Al) and give rise to a thin titania shell. In this way, MIL-100(Al) can act as a template, allowing the preparation of titania samples with high SSA and photocatalytic activities. The same procedure can be applied with TiO$_2$@HKUST to produce rutile nanoparticles. Such results will be reported in a future work.

Conclusions

This work reported the first time the preparation of aluminum-based MOFs decorated with TiO$_2$. A copper trimesate (HKUST-1) was likewise modified for comparative purposes. The MOFs were initially prepared by hydrothermal treatment and showed specific surface areas up to 1787 m$^2$ g$^{-1}$ and were subsequently submitted to a sol–gel modification step, where titania nanoparticles were grown on their surface. Anatase nanoparticles were observed anchored on MIL-100(Al) after this step; the titania concentration on this sample was around 68 wt.%. This approach led to materials with narrower bandgaps (3.70 eV against 3.27 eV) and a higher capacity to degrade MB ($k_{\text{app}} = 1.29$ h$^{-1}$), IBP ($k_{\text{app}} = 0.37$ h$^{-1}$) and DIC ($k_{\text{app}} = 0.21$ h$^{-1}$) under UVA illumination in comparison to MIL-100(Al). It was observed that TiO$_2$@MIL-100(Al) gave rise to a significant concentration of ROS as a function of time, revealing the promising photoactivity of this material. These findings reveal that MIL-100(Al) is a promising matrix to anchor semiconductors nanoparticles and give rise to efficient photocatalysts. On the other hand, the sol–gel modification of HKUST-1 caused a major change in its pore structure, leading to the formation of rutile nanoparticles on a non-porous Cu$_2$(BTC)(OH)(H$_2$O) phase. The structural collapse of HKUST-1 during the hydrothermal sol–gel step led to fewer sites for the heterogeneous nucleation of titania nanoparticles and a low concentration of TiO$_2$ on the composite prepared (around 9 wt.%). Despite this behavior, the sol–gel modification of HKUST-1 was beneficial to its photoactivity, increasing the photodegradation rates evaluated for MB (0.05 h$^{-1}$ vs. 0.29 h$^{-1}$), DIC (negligible vs. 0.03 h$^{-1}$), and IBP (0.01 h$^{-1}$ vs. 0.02 h$^{-1}$).

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Data availability

The data supporting the results of this study are all the authors’ findings and are not available elsewhere.

Declarations

Conflict of interest

The authors declare that they have no conflict of interest.

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