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ARTICLE INFO ABSTRACT Keywords: Adsorption Photocatalytic Degradation

13In this study, a facile one-pot method was developed to

create hierarchical porous M- ZIF- 8 by utilizing NaOH as a defecting agent. The as-synthesized material comprising macroporous and mesoporous and exhibits hierarchical porosity. TiO₂ (anatase) with different mass ratios (5%, 15%, and 25%) were immobilized into M- ZIF- 8 to combine the synergism of adsorption and photocatalytic oxidation. Five percent of TiO₂ immobilized in M- ZIF- 8 gave the best adsorption and photocatalytic degradation. The adsorption kinetics and isotherms of CV on M- ZIF- 8 were also evaluated to validate the adsorption capability of M- ZIF- 8. After four consecutive experiments, the adsorption and

27photocatalytic performance of M- ZIF- 8@TiO₂ to

degrade CV slightly decreased. 1. Introduction Advanced Oxidation Processes (AOPs) are regarded as one of the most-efficacy techniques in hazardous substances elimination from wastewater compared to other commonly employed wastewater treatment processes (Miklos et al., 2018). AOPs offer several advantages, including facile operation at or near ambient pressure and temperature and transform roughly all the contained organic contaminants in effluents into less hazardous substances (Kanakaraju et al., 2018). Various processes such as Fenton (Lu et al., 2021) and photo-Fenton catalytic reaction (Vorontsov, 2019), processes using H₂O₂ or UV-Irradiation (Yang et al., 2017), as few instances of AOPs, counts as the efficient techniques through hydroxyl radical's production which oxidizes non-selectively extensive range of organic contaminant in wastewater. The utilization of photocatalytic degradation under UV/Visible irradiation appears as a green technique in wastewater treatment, particularly in dye degradation. Variety photocatalyst substances such as TiO₂ (Chen

17et al., 2020), ZrO₂ (Chen et al., 2020), and ZnO (Ong et al., 2018

) have been utilized for pollutants elimination. TiO₂ is the most promising photocatalysts among diverse photocatalysts due to superior photostability, minimum production cost, excellent intrinsic catalytic activity under UV-Irradiation, and non-toxic and harmful towards both environment and humans (Abdi et al., 2019). Nevertheless, the photocatalytic activity of pure TiO₂ experienced two significant shortcomings: firstly, pure TiO₂ can limit the influence of catalytic activity on account of the nanospheres aggregation; Secondly,

28rapid recombination of photo-induced electrons and holes weaken the

photo- induced redox reaction. Thereby, how to tackle the TiO₂ aggregation and dwindled the recombination rate of photo-induced electrons and holes emerged as our research focus. Incorporating the semiconductor towards other porous materials may overcome the major drawbacks and enhance photocatalytic performance. One of the engineered materials, namely

13 **metal-organic framework (MOF)**, has **received significant attention**

14 **owing to the high surface area**, high porosity, **and structural**

versatility. MOFs are inorganic-organic hybrid materials with the porous framework constructed by self-assembly between the metal cluster or polynuclear secondary building units (SBUs) and organic ligands (Joseph et al., 2019). Until now, over five thousand diverse MOFs structure have been constructed on record at Cambridge Crystallographic Data Centre (Furukawa et al., 2013), showing outstanding performance towards several fields such as adsorption, catalyst, chemical separation, gas storage, and sensors. However, regardless of the structural flexibility and rich chemistry, mostly the recently published MOFs having microporous structure (pore *

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6 **2021 Elsevier B.V. All rights reserved.** sizes <1

nm) consequently restraint the diffusion of the bulky molecules and limits the accessibility of open channel or MOFs active sites (Guan et al., 2018). Hence, the methodology of enlarging the pore size for

18 **mass transfer** improvement **and** refine **the accessibility of**

active sites are highly required. Various processes

18 **have been developed to** synthesize **mesoporous MOFs**

7 **such as ligand extension**, ligand **mixing, post-treatment, and templating**

techniques (Guan et al., 2018). Regrettably, most of the mentioned methodology requires complex techniques, long-time processes, and high-cost reagents, hindering practical and production feasibility. For

ligand mixing and ligand extension methods, it required diverse ligands to elongate the

7distance between metal centers which induce **complexity and** unpredictability of as-synthesized **MOFs**: the complex **fabrication, cautious activation**, and structural **metastability**

. Thereby, it is required a simplified method to introduce mesoporous structure in micropores of MOFs. Different approaches have been advanced to simplify introducing the mesopores into imidazolate-based MOFs with microporous structure, Zeolitic Imidazolate Framework (ZIF-8). In general, ZIF-8 is a hybrid engineered material with a porous structure analogous to zeolites constructed through 4-connected nets of tetrahedral units where Zn^{2+} as metal cluster coordinated to N atoms in diatopic imidazolate anions. ZIF-8 presents a sod topology consisted of 1.16 nm cages connected through 0.34 nm six-membered windows (Fig. 1(a and b)). Zhang's groups (Zhang et al., 2015) developed sequent synthesis through nanoparticle encapsulation followed by the etching method to develop the mesopores structure of ZIF-8. Jing et al. (Jing et al., 2018) utilized polystyrene

2as a template to construct hierarchical **ZIF-8 with** micro-, meso-, **and macropores**

structure. Li's and Jhung's groups (Wu et al., 2014; Jung et al., 2015) fabricate

7hierarchical **ZIF-8 with micro-and mesopores**

structure by utilizing cetyltrimethylammonium bromide (CTAB) amino-acid L-histidine as co-template. Chou et al. (Chou

18et al., 2015) **put forward a double**

solvent mediate overgrowth mechanism for the

18hollow and mesoporous structure of **ZIF-8** construction. **A**

work by Chen et al. (Chen et al., 2019) through facile one-pot synthesis with the utilization of poly(diallyl dimethylammonium chloride) (PDDA) as the structure-directing agent to construct hierarchical meso-,macroporous of ZIF-8 porosity. Unfortunately, all of this method required expensive reagents and relatively complicated procedures to utilize. In this work, we successfully develop facile synthesis through a one- step approach method of construct hierarchical ZIF-8 with meso-,mac- roporous structure with the addition of sodium hydroxide (NaOH). This approach has been in line with tailoring MOF materials for photocatalytic activity through hosting the TiO_2 materials in a porous framework. Incorporating TiO_2 into zeolites or coating TiO_2 with other substances and similar techniques has been widely adopted recently (Wang et al., 2014; Xu et al., 2018). The utilization of covered TiO_2 NPs frequently diminishes the catalytic activity owing to limited access to- wards dissolved organic dyes (Chandra et al., 2016). Meanwhile, Immobilization and encapsulation techniques of TiO_2 NPs into inorganic substances provide more effective catalytic activity despite having sta- bility issues with zeolites as typical inorganic hosts (Liu et al., 2014). Since ZIF-8 exhibits thermal and chemical stability with mesoporous structure, this material was chosen as the host for TiO_2 encapsulation. Photocatalytic activity of ZIF-8 and I ts nanomaterials composite has been widely explored

utilizing UV-Irradiation, for instance: ZnO@ZIF-8 (Akbari Beni et al., 2020; Yang et al., 2018), Ag/AgCl@ZIF-8 (Fan et al., 2018), Pt@ZIF-8, and CuInS₂@ZIF-8 (Liu et al., 2019). It was observed, the M-ZIF-8@TiO₂ composite provides synergism catalytic activity through simultaneous adsorption and photocatalytic degradation. Due to its mesoporous

2structure of M-ZIF-8, M-ZIF-8

presents excellent adsorption ability by improving the active site accessibility and molecular diffusion to extend the contact time between catalyst and crystal violet (CV) and elevate the ability of CV degradation. Moreover, TiO₂ was homogeneously incorporated into the M-ZIF-8 pore and constructed

27N-Ti-O bond under facile synthesis treatment

, preventing fast recombination of the electron-hole pairs and aggregation of TiO₂ nanomaterials photocatalytic system. Because of the unique porosity of the M-ZIF-8@TiO₂ composites and the chemical bonded M-

10ZIF-8@TiO₂, this composite improved the photocatalytic activity of

crystal violet degradation while maintaining its thermal stability and crystallinity after post-modification.

192. Materials and method 2.1. Materials The chemicals

involved in this research including zinc sulphate heptahydrate (ZnSO₄·7H₂O) (CAS:7446-20-0, 99.295%purity trace metal basis), 2-Methylimidazole (CAS: 693-98-1; 99%), sodium hydroxide (NaOH) (Analytical Reagent (AR) Grade; CAS: 1310-73-2; ≥ 98.5% purity) and Titanium (IV) oxide (TiO₂) (CAS: 1317-70-10) anatase grade, 99.8% trace metal basis), crystal violet (C₂₅H₃₀N₅Cl) (CAS:548-62-9; ACS Reagent ≥ 90.0% anhydrous basis, isopropyl Fig. 1. Chemical structure of ZIF-8; (a) tetrahedron building units of M-ZIF-8 (Zn(Hmim)₄ Tetrahedron); (b) M-ZIF-8 architecture manifests cages with diameter 1.16 nm and six-membered windows with 0.34 nm. Molecular formula: Zn – Red, C – Gray, N – Blue. Notes that H atom does not appear in the structure figure to simplify the display of ZIF-8 Structures. (

19For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article

.) alcohol (IPA) (CAS:67-63-0; ACS Reagent ≥ 99.5%), P-benzoquinone (C₆H₄O₂) (CAS:106-51-4; Reagent Grade ≥ 99.5%), carbon tetrachloride (CCl₄) (CAS: 56-23-5; Reagent Grade ≥ 99.9%) and ammonium oxalate monohydrate (NH₄)₂C₂O₄·H₂O) (CAS:106-51-4; ACS Reagent ≥ 99%).

32All chemicals were acquired from Sigma Aldrich, Singapore, and were subsequently utilized without any further purification. 2.2. Fabrication of Macro-/Mesoporous ZIF-8 (M-ZIF-8) and M-ZIF

- 8@TiO₂ composite The M- ZIF- 8 were assembled in an aqueous phase by simply mixing a solution of ZnSO₄·7H₂O and 2-Methyl Imidazolate with the addition of NaOH. Initially, a certain quantity of ZnSO₄·7H₂O

7 was dissolved in 5 ml of DI water to create a 0.84 M solution

. Subsequently, 16 ml solution (3.00 M) comprising of 2-methyl imidazole (Hmim) were mixed with 1.6 ml of solution A and the addition of 0.2 ml NaOH solution (0.1 M). Further, the deionized water was added to the mixture until the total volume of the solution was 50 ml, and the mixture was stirred at room temperature for one hour. The as-synthesized product was isolated by centrifugation, washed by DI water until the supernatant achieved neutral pH. The solid was evacuated

7 and dried under vacuum at 60 °C for further

composite preparation. A photocatalytic agent, TiO₂,

7 was introduced into the system for preparing M- ZIF- 8. A specific volume of TiO₂ solution

was added in the as-mixed solution of M- ZIF- 8 according to the weight ratio of TiO₂ (5%, 15%, and 25%), and the stirring was continued for one h. Prior to the synthesis, TiO₂ solutions were made by immersing 2 gr TiO₂ into 5 ml methanol assisted with ultrasonication for 1 h. The schematical procedure is depicted in Fig. 2(b). Pristine

23 ZIF-8 and ZIF-8@TiO₂ (5%) were

synthesized according to similar synthesis steps without NaOH addition. 2.3. Characterization of

3 M- ZIF- 8 and M- ZIF-8@TiO₂ M- ZIF- 8 and M

- ZIF8@TiO₂ composite

13 were characterized using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), nitrogen (N₂) adsorption – desorption isotherms, and

Fourier transforms infrared (FTIR) spectroscopy. The powder X-ray diffraction patterns of M- ZIF- 8 and M- ZIF8@TiO₂ were determined using

5 Bruker D2 Phaser diffractometer equipped with a Cu K α radiation source (λ = 0.15406 nm

) in the 2θ range of $5 - 50^\circ$ and a scan rate of $0.05^\circ/\text{s}$. SEM images were obtained by

1 JEOL JSM-6500F field emission SEM at

an accelerating voltage of 15.0 kV and a working distance of 9.7 mm. All solid

1 samples were coated with thin layer platinum before the

surface topography analysis using SEM. N_2 sorption isotherms at 77 K were measured by

2 Micromeritics ASAP 2020 analyzer. Before the measurements, the **samples were degassed at 200 C for 12 h**

under a vacuum of $4000-500 \text{ cm}^{-1}$ using Shimadzu 8400S spectrometer through the KBr environment. FTIR spectra were recorded at a range wavenumber of pellet technique.

4 X-ray photoelectron spectroscopy (XPS) was carried on VG Thermo ESCALAB

Mark II to evaluate the elemental states of M-ZIF-8@TiO₂. The UV diffuse reflectance spectra (DRS) were measured

4 on a UV-vis spectrophotometer (Hitachi U-4100) across a 200-800 nm wavelength range

, with BaSO₄ as the reflectance standard. A conventional three-electrode cell comprising a working electrode, a Pt counter electrode, and a standard Ag/AgCl electrode reference electrode was used to evaluate transient photocurrent density on a CHI660B Fig. 2. Schematic

14 procedure of (a) M-ZIF-8 and (b) M-ZIF-8

@TiO₂ composites synthesis. Electrochemical Workstation (Shanghai, China). The electrolyte was a solution containing 0.5 mol/L Na₂SO₄.

28 A 0.5 mol/L Na₂SO₄ aqueous solution was used to make the electrolyte

. Electrochemical impedance spectra (EIS) were performed at the open-circuit potential in 0.5 mol/L potassium ferricyanide/potassium ferrocyanide solution. The electrode was subjected to a 5 mV sinusoidal AC perturbation with a 0.5-100000 Hz frequency range.

92.4. Adsorption and photocatalytic degradation experiments The present work studied **the** performance of

adsorption/photo-catalytic degradation of

2ZIF-8/ZIF-8@TiO₂ and M-ZIF-8/ M-ZIF-8

@TiO₂

9to remove toxic organic dye CV from aqueous media. The adsorption experiment was conducted without UV light

, while photocatalytic degradation was carried out in

1a UV lamp as the light source. The adsorption and photodegradation processes were conducted isothermally with an initial concentration of

crystal violet 200 ppm. In the experiment, 1 g/L of

31M-ZIF-8/or M-ZIF-8@TiO₂/or ZIF-8/or ZIF-8

@TiO₂ was dispersed CV solution. The

1flasks containing the mixture were placed in a thermal-controlled shaking water bath (Memmert WB- 14) with

/without UV irradiation during the experiments. Initially, the

1adsorption experiments were conducted in the dark

condition. After the equilibrium point of adsorption had been reached, the photoirradiation process was conducted on the mixture using UV light at 360 nm. The experiments were

9conducted at room temperature (30 C). The total adsorption and photodegradation time was 24 h

. After the

1adsorption and photocatalytic degradation processes, the

solids were separated from the mixture by centrifugation (

1 Heraeus Labofuge 200) at 4900 rpm for

10 mins. The

1 initial and equilibrium concentrations of CV were determined by UV-Visible Spectrophotometer (UV mini 1240 Shimadzu) at the maximum wavelength

of CV (590 nm). The amount of CV adsorbed by ZIF-8 and ZIF-8@TiO₂

1 at equilibrium condition was determined by equation (1) as

follows: $q_e = (C_o - C_e) m \times V$ (1) Where q_e is the amount of CV adsorbed at equilibrium (mg/g), C_o is the concentration of CV

1 in the liquid phase at initial condition

(

11 mg/L), C_e is the concentration of CV in the

liquid phase at equilibrium condition (

5 mg/L), V is the volume of CV solution (L), and m is the mass of adsorbent (g).

3. Characterization **The**

surface morphology and topography

2 of M- ZIF- 8 and M- ZIF- 8

@TiO₂ (5%) was evaluated through scanning electron microscopy (SEM). SEM images exhibit that M- ZIF- 8 has a non-uniform structure with a truncated rhombic dodecahedron shape (Fig. 3). Fig. 3(b) manifests the SEM image of the M- ZIF- 8@TiO₂ composite, flower like morphology (Zhong et al., 2020) was obtained after incorporating TiO₂ into ZIF-8 with no-obvious structural disintegration of ZIF-8. However, no-substantial TiO₂ was visible in the SEM Image, but the elemental composition of M- ZIF- 8@TiO₂ (5%) composite by SEM-EDX indicates the presence of TiO₂. As shown in Table 1,

16 five elements (C, N, Ti, O, and Zn) were discovered in the composite, which further specifies the

success of TiO₂ integration towards MOFs. Moreover, the EDX mapping also detected

11 **five elements (C, N, Ti, O, and Zn)**, as seen in Fig. 3(c). **The**

elemental distributions of C, O, Ti, Zn, and N are represented by green, red, yellow, blue, and purple. The presence of the elements Ti and O on the surface of the ZIF-8@TiO₂ composite in the mapping diagram suggests the successful distribution of TiO₂ nanospheres. The phase purity and crystallinity of M-ZIF-8, M-ZIF-8@TiO₂ (5%) Table 1

11 **Elemental Composition of M-ZIF-8@TiO₂ based on**

SEM-EDX. %Elemental Composition M-ZIF-8 M-ZIF-8@TiO₂ C 49.73 N 30.23 Zn 12.94 O 7.1 Ti – 48.29 27.27 11.8 9.38 3.25 Fig.

303. **Scanning Electron Microscopy (SEM) of M-ZIF-8 (a**

) and M-ZIF-8@TiO₂ (b); (c) SEM-EDX Mapping of M-ZIF-8@TiO₂. and TiO₂ (anatase) were evaluated by X-ray diffraction (XRD) (Fig. 4 (a)).

12 **According to the XRD diffractograms**, the **synthesized**

M-ZIF-8

12 **showed major characteristic reflections of the M-ZIF-8 sodalite structure at 2θ angles of 7.5°, 10.6°, 12**

.9°, 14.9°, 16.6°, and 18.2°, which attributed to the ZIF-8 planes including (220), (311), (422), (511), and (440) respectively and

12 **were consistent with the ZIF-8 single-crystal XRD pattern**

based on CCDC 602,542 (Tran et al., 2011). Meanwhile, the characteristic peak of TiO₂ was identified at 25.4°, 47.9°, 53.9°, 55.9°, and 62.7° which correspond to the (101), (200), (105), (211), and (204) crystal planes of TiO₂ (anatase) and matched with the TiO₂ simulated card (ICSD-50447) (Zhang et al., 2019). For the M-ZIF-8/TiO₂ (5%) composite, the XRD pattern simulated the major diffraction peaks of ZIF-8, with insufficient evidence of TiO₂ characteristic peaks owing to the weak intensity of the peak of TiO₂ (anatase) nanoparticles. Therefore, SEM and SEM-EDX were used to validate the XRD results further.

10 **Fig. 4(b) shows the N₂ adsorption – desorption isotherms of the**

M-

3ZIF-8 and M-ZIF-8@TiO₂, respectively. The porous structure characteristic of M-ZIF-8 and M-ZIF-8@TiO₂ are listed in

Tables 2 and 3. The

11N₂ sorption isotherm of M-ZIF-8

at 77 K exhibits Type I(a)/II isotherm (Lunardi et al., 2021). The swift

21N₂ uptake at a low relative pressure area ($P/P_0 < 0$

.05) indicates the MOF framework having a narrow microporous structure. Meanwhile, the subsequent step N₂ up-take at a high relative pressure ($P/P_0 > 0.95$) indicates the existence of > large mesoporous and macroporous in MOF structures. The presence of large mesopores and macropores in the MOF structure can assist TiO₂ encapsulation in the MOF and facilitate the mass transport of CV to the internal

2structure of the M-ZIF-8@TiO₂. The M-ZIF-8

possesses

18a high BET surface area (2151 m²/g

), while incorporating TiO₂ on the porous structure of M-ZIF-8 reduced the composite surface area to 854 m²/g. The decline in the composite porosity implies proper confinement of TiO₂

2on M-ZIF-8. Fig. 4(c). shows the

2FTIR spectra of M-ZIF-8 and M-ZIF-8

@TiO₂. Vibration bands indicated the typical characteristic for ZIF-8 at 1427 cm⁻¹, 1419 cm⁻¹, and 995 cm⁻¹ that are assigned to C-N stretch, the

25bands at 1147 cm⁻¹, 1143 cm⁻¹, 1311 cm⁻¹, and 1308 cm⁻¹ are attributed to

imidazole bending, while the intense band at 420 cm⁻¹ are associated with the Zn-N stretch (Hu et al., 2011). In addition,

27the typical vibration of the N-Ti-O bond was shown in

568 cm⁻¹, which demonstrates the successful growth of TiO₂ confined in ZIF-8 (Li et al., 2020; Zeng

29et al., 2016). **The presence of the N-Ti-O bond**

indicates that the formation of ZIF-8@TiO₂ is not a simple physical mixing of the two chemical substances but a combination of chemical bonds. The

16XPS survey spectrum of the M- ZIF- 8@TiO₂ (5%) composite

was shown in Fig. 5, indicating five elements, namely N, Ti, C, O, and Zn.

4In the C 1 s spectra, Fig. 5(a) indicates the appearance of

C-C, and C-N coordination at 284.6 eV and 285.1 eV. Fig. 5(d) illustrates the O1s XPS spectrum of the composite. The major fittings peaks reveal the binding energy of Ti-O and Zn-OH at 529.8 and 531.4 eV, which also confirm TiO₂ and ZIF-8 constructed the prepared composite. From Fig. 5(b), the XPS spectrum of Zn 2p from M- ZIF- 8@TiO₂ (5%) revealed two peaks at 1021.3 eV and 1044.5 eV, which indicated the

10Zn 2p_{3/2} and Zn 2p_{1/2}

binding energies (Cardoso et al., 2018). As present in Fig. 5(

4b), the Ti peaks at 458.4 eV and 464.1 eV

, which implies oxidation states Ti⁴⁺ in 2p_{3/2} and Ti 2p_{1/2} binding energies were displayed by two significant M- ZIF- 8@TiO₂ (5%) composite. Fig. 5(c) represents the N1s XPS spectrum. The peaks at 400.3 eV represent the binding energy of C-NH- and imidazole groups, while 399.6 eV peaks reveal N-Ti-O bonds in the composite. The N atoms in imidazole groups coordinated to replace the oxygen atoms in TiO₂, which verified the chemical bonding between TiO₂ and ZIF-8 nanoparticles (Pi

29et al., 2018). **The presence of N-Ti-O**

coordination may illustrate the possibility of electron transfer from TiO₂ to ZIF-8, catalyzing photogenerated charges and lowering the recombination rate compared to its counterpart. In order to justify the statement, photoluminescence (PL), transient photocurrent response and electrochemical impedance, and UV-diffuse reflectance spectra were employed for further validation. UV-diffuse reflectance spectroscopy was utilized to determine the light absorption ability of the

14M- ZIF- 8, TiO₂, and M- ZIF- 8@TiO₂ (5%). As presented in

Fig. 6, M- ZIF- 8 has the optimum absorption wavelength at 228 nm, indicating M-

16ZIF- 8 can only respond to the UV- light

irradiation while TiO₂ intensely responds to the visible irradiation since the measured optimum wavelength at 370 nm. When the integration of M-ZIF-8 and TiO₂ occurs, the composites reveal a broader absorption region that extends into the visible area owing to tight interaction between M-ZIF-8 and TiO₂, which ameliorate the composite light absorption capability and make the absorbed intensity in UV regions stronger. The optical band gap of the-as-synthesized material

4can be measured using the Tauc Plot by modified the UV-DRS curve

into $(\alpha h\nu)^2$ versus $h\nu$. The

10absorption coefficient, Planck constant, light frequency, proportionality constant, and

bandgap are represented by h , ν , A , and E_g . The band gaps of the samples would be determined by $(\alpha h\nu)^2$ versus $h\nu$ (the absorbed light energy) (Zhong et al., 2020). The

4x-axis intercept of an extended tangential line from the linear portion of the curve

was used to calculate the E_g value. Fig. 6(b) exhibit the estimated bandgap energies

11of M-ZIF-8, TiO₂ and M-ZIF-8@TiO₂ that are

5.14 eV, 3.33

10eV and 2.98 eV respectively. The dramatical decrease of

bandgap value indicates the applicability of the composites for light-harvesting in the visible range scope and ameliorates the photocatalytic system's efficiency. Moreover, the measurement of the valence band and conduction band was also crucial to assessing the photocatalytic applicability. The linear extrapolation of the VB XPS spectrum leading edges to the base-line was utilized to evaluate the VB position of M-ZIF-8@TiO₂ (5%). As evaluated, ~2.1 eV was exhibited as the valence band of M-ZIF-8@TiO₂ (5%) while the CB position was measured on - 0.87 eV, which is acquired from (EVB - E_g). For CV and VB pristine TiO₂ and ZIF- Fig. 4. Characterizations

11of the M-ZIF-8 and M-ZIF-8

@TiO₂ 5%. (a) Powder XRD

2patterns of the M-ZIF-8 and M-ZIF-8

@TiO₂ as well as the simulated diffraction pattern from CCDC-602542 (ZIF-8) and ICSD-50447 (TiO₂-Anatase). (b) Nitrogen adsorption - desorption

2 Isotherms of M-ZIF-8 and M-ZIF-8@TiO₂ 5% and at 77 K along with the

Barrett-Joyner-Halenda (BJH) plot; (c)

2 FTIR spectra of the M-ZIF-8 and M-ZIF-8

@TiO₂. Table 2 Comparison of Several Porous Structure of mesoporous/macroporous ZIF-8. Sample Synthesis Method of Mesoporous/Macroporous Structure SBET (m²/g) Pore Volume Average pore Diameter References g) (cm³/g) (nm) M-ZIF-8 HpZIF-8 Mesoporous ZIF-8 HZIF-8 Mesoporous ZIF-8 NaOH Addition Structure Directing of PDDA (poly(diallyl dimethylammonium chloride) utilization of cetyltrimethylammonium bromide (CTAB) and amino-acid L-histidine as co-template Polystyrene as directing template agent Double solvent mediated overgrowth 2151 1.4998 242 – 1134 1.30 1108 – 1276 – 124.66 – – 50–350 250 This study (

25 Chen et al., 2019) (Jung et al., 2015) (Jing et al., 2018) (Chou et al

, 2015) Table 3 Comparison of Several Porous Structure of ZIF-8@TiO₂. Sample SBET (m²/g) Pore Volume (cm³/g) Average pore Diameter (nm) References M-ZIF-8@TiO₂ (anatase) ZIF-8@TiO₂ 854 556.809 0.6023 0.408 25 2.932 This Study (Chen et al., 2019) ZIF-8@TiO₂ 668 0.81 1.2 (Zhang et al., 2019) ZIF-8@TiO₂ 253.882 – – (Chandra et al., 2016) 8, the following empirical formula was used (Zhang et al., 2019): $EVB = X - E_e + 0.5E_g$ $ECB = EVB - E_g$ (2) (3) Where variable “X” stands for the semiconductor’s electronegativity, calculated based on the geometric mean of Mulliken electronegativity values of its constituent atoms. The arithmetic mean of the initial ionization energy and the first electron affinity represent the Mulliken electronegativity of an element (

45.81 eV for TiO₂ and 2.36 eV for ZIF-8

) (Zhang et al., 2019). E_e

8 is the energy of free electrons on the hydrogen scale

with a constant value of 4.5 eV vs. NHE (Wei et al., 2017), and E_g denotes the samples’ bandgap energy measured by UV-DRS. Table 4. Represents E_g , EVB , X and ECB values of the composites and its counterpart. In photocatalytic application, photoluminescence (PL) has been frequently utilized to evaluate charge carrier recombination rates between each sample. In the previous XPS characterization, it was reasonable to hypothesize the possible charge carrier migration path that establishes between TiO₂ and ZIF-8 (Zhang et al., 2019). Therefore, PL was applied to evaluate the charge carrier phenomenon. Fig. 6(d) shows the PL spectrum in which the PL intensity of TiO₂ is higher than the M-ZIF-8@TiO₂ (5%). The higher PL intensity indicates the greater possibility of the photogenerated carrier recombination in PL spectra. Pure TiO₂ provides a higher rate of electron-hole recombination. However, further incorporation of M-ZIF-8 has quenched the strong PL intensity, which indicates that the M-ZIF-8 addition effectively divides the

30 **electron-hole pairs** by blocking **the recombination of** the photo-generated **electron hole pairs**, which implies **the**

existence of a special path for carrier conveyance between TiO₂ and M-ZIF-8. Due to lower charge carriers' recombination rates, more electrons can be engaged in the photoreduction process. Fig. 5. The

10 **high-resolution XPS spectra for the Ti2p (a), Zn2p (b), C1s, (c), N1s (d), O1s (e) regions**

of M-ZIF-8@TiO₂ (5%). Fig. 6. (a). UV-Diffuse Reflectance Spectra of

3 **M-ZIF-8, M-ZIF-8@TiO₂ (5%) and TiO₂; (b). M-ZIF-8, M-ZIF-8**

@TiO₂ (5%) and TiO₂ optical band gap energy graphs; (c) the XPS Valence Band Spectrum For M-ZIF-8@TiO₂ (5%); (d) PL spectra; (e) Electrochemical impedance spectra and; (f) Photocurrent intensity

11 **of M-ZIF-8, TiO₂ and M-ZIF-8**

@TiO₂ (5%). Table 4 Summary of electronegativity χ , band gap energy E_g (in eV), energy positions of band edges (EVBM and ECBM, in eV) of composite and its counterpart. Materials X (eV) a E_g (eV) EVB (eV) b ECB (eV) b ZIF-8 2.36 5.14 0.43 - 4.71 TiO₂ M-ZIF-8@TiO₂ 5.81 n.d. 3.33 2.97 2.98 2.1 - 0.35 - 0.87 Electrochemical Impedance Spectroscopy (EIS) and photocurrent studies of the as-synthesized samples were carried out to further comprehend composites' charge transfer property on the photocatalytic activities.

4 **Electrochemical impedance spectroscopy could visualize the photogenerated electron-hole pairs separation and interfacial charge transfer resistance**

(EIS). The

4 **EIS Nyquist plot would possess an arc shape**

when charged migration was present (Zhang et al., 2019). A smaller arc radius indicated higher charge transfer capabilities on the plot, which aided in separating photogenerated electron-hole pairs. Fig. 6(e) manifests the torque samples EIS spectrum. The

4 **arc radius of pristine TiO₂ and M-ZIF-8@TiO₂ (5%) are smaller than**

M-ZIF-8. This result revealed that composite fabrication could increase the electron transfer speed and efficiency of M-ZIF-8 and further ameliorate photocatalytic activity. Fig. 6(f) presents the photocurrent intensity of three materials. The M-ZIF-8 photocurrent response was the weakest of all. Although pristine

TiO₂ had the maximum photocurrent density, their intensity faded over time after prolonged exposure to irradiation. The photocurrent intensity of the M-

23 **ZIF-8@TiO₂ (5%) composite is higher than that of**

M- ZIF- 8, and it remains consistent over time, indicating that the composite is more stable than TiO₂. The reduction of electron-hole recombination achieved by incorporating TiO₂ onto ZIF-8 further increased photocatalytic efficacy. 4. Simultaneous adsorption and photocatalytic degradation

11 **of M₁ZIF₁8 and M₁ZIF₁8**

@TiO₂ 4.1. Synthesis mechanism of NaOH

2 **on M- ZIF- 8 and M- ZIF- 8**

@TiO₂ formation As analyzed, the morphological and porous structure clearly induced by the presence of NaOH during the synthesis of

2 **M- ZIF- 8 and M- ZIF- 8@TiO₂ (5%). Theoretically, the morphological structure of M- ZIF- 8**

is affected by several factors such as solvent, temperature, stoichiometric ligand/metal molar ratio, which

12 **can be attributed to the competition of ligand hydrolysis against**

the M- ZIF- 8 formation (Jian et al., 2015). Hydrolysis in aqueous media and rapid synthesis of M- ZIF- 8 limits the excess ligand to undergoes deprotonation and retard the nuclei construction. The role of NaOH as the basic compound is to increase the deprotonation rates of ligand. Since the

12 **excess ligand produced from reverse hydrolysis is different from the**

deprotonation rates of NaOH, resulting in an immature morphology of M- ZIF- 8. Beneficially, this also can be the reason for the formation of mesoporous and microporous structures in M- ZIF- 8, since the idea of mesoporous or macropores formation is the competition of ligand with other moieties or linker removal in structural framework to expand the size of pores. The mechanism formation of M- ZIF- 8 is divided into three steps: hydrolysis, coordination, and deprotonation (Fig. 7(a)). The first step of M- ZIF- 8 formation through coordination of Zn²⁺ ions into deficient electron of pyridinic nitrogen of imidazole linker molecules which further induce the Zn(Hmim)_n²⁺ (1 ≤ n ≤ 4) complex formation (Bus-tamante et al., 2014). Subsequently, the complexes begin to release the proton via

12 **deprotonation reaction with the assistance of basic species such as ammonia, excess linker, ion acetate (OAC**

), which in this case, – the basic species was NaOH (Malekmohammadi et al., 2019). In the absence of these basic moieties, the deprotonation of ligand and the formation of M– ZIF– 8 nucleus un-initiated in water since the pKa relatively high (~15–15.7). The solvent itself (in this case was water) acts as a mold to regulating the M– ZIFs structure via non-covalent

17**Fig. 7. (a) Mechanism formation of M– ZIF– 8, and (b**

) defective formation on M– ZIF– 8 structure. coordination for bridging and pore stabilization throughout the cage's growth (Moh et al., 2011). Moh et al. (Moh et al., 2011) have investi- gated this phenomenon, and they found hydrogen linkage betwixt of the head of solvent consists of electronegative oxygen and the pyrrolic hydrogen of imidazole ring in linkers throughout the M– ZIF– 8 formation. Generally, the mechanism

34**formation of M– ZIF– 8 in the** solution required **the** deprotonation **of Hmim**

(mim ions) to bridge the zinc ions – to produce building units. However, the mechanism of M– ZIF– 8 formation in water relatively complex because ligand strongly undergoes hydrolysis reaction in an aqueous solution. Initially, the production of (H₂mim) begins with the reversible hydrolysis of the linker, and since + the Hmim only present two structural isomers in water, including Hmim and (H₂mim) , the pH of the solution tend to increase. Then simulta- + neously, two phenomena occurred, namely complexation between zinc ions and linkers and reverse hydrolysis of linkers, which resulted in a drastic decrease in the pH of the solution because the hydrolysis reaction equilibrium shifted to the left side and the rapid use of Hmim during the coordination process. This is the purpose of increasing ligand to metal ratio to fulfill the requirement of deprotonation steps in aqueous solu- tion to achieve higher M– ZIF– 8 phase purity since the intermediate product of Zn(Hmim)_n²⁺ (1 ≤ n ≤ 4) (pKa 10.3) has lower deprotonation compared to Hmim (Cravillon et al., 2011). Eventually, the excess of Hmim can act as a deprotonation agent for protons cation removal to enable Zn(Hmim)₂⁺ complexation and generate M– ZIF– 8 crystals. With the adjustment of time, the reaction may induce the morphology transformation of ZIF-8, which is caused by the different deprotonation steps, and the rate of excess Hmim and NaOH leads to the two types of M– ZIF– 8 morphology formation. The truncated rhombic dodecahedron is likely generated from the deproto- nation and rearrangement of complex coordination between zinc ions and excess ligand. With NaOH as a deprotonation agent and a high ligand to metal ratio, the rapid nucleation rate also increases, which might hinder the M– ZIF– 8 growth significantly, causing the defective formation of ZIF-8 (Cravillon et al., 2011). Therefore, the defective formation and rearrangement of linkers in M– ZIF– 8 induce macro- porous/mesoporous structure (Fig. 7(b)). In comparison, this study provides a higher porous structure compared to those published

23**ZIF-8/ TiO₂ composites and mesoporous ZIF-8 (shown in**

Tables 2 and 3). Therefore, the addition of NaOH before the synthesis

2**of M– ZIF– 8 and M– ZIF– 8**

@TiO₂ could increase the pore diameter and the surface area. 4.2. Crystal violet isotherm and kinetic adsorption through

2**M– ZIF– 8 and ZIF-8 In**

this study, Freundlich and Langmuir

1 were employed to correlate the experimental adsorption data

of CV onto

3 M-ZIF-8 and ZIF-8. The mathematical expression of

the Freundlich model is shown below (Al-Ghouti and Da'ana, 2020): $q_e = K_F \times C_e^{1/n}$ (4) where q_e is the

1 amount of dyes adsorbed on the solid at equilibrium condition, C_e is the equilibrium concentration

, and K_F is Freundlich constants (

5 mg/g (mg/L)⁻ⁿ, n is the heterogeneity of the system. The

mathematical form of the well-known Langmuir isotherm is expressed as (Al-Ghouti and Da'ana, 2020): $q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ (5) Parameters q_{max} and K_L

7 are the Langmuir constants, representing the maximum adsorption capacity (mg/g) and the

adsorption affinity (L/mg), respectively. The experimental adsorption isotherm data of CV onto M-ZIF-8 and ZIF-8 based on Freundlich and Langmuir plots are given in Fig. 8(a). The Freundlich and

1 Langmuir equation parameters obtained from the fitting of the experimental data are given in

Table 5. From Fig. 8(a) and Table 5,

1 it is proven that the Langmuir equation could represent the experimental data better than the Freundlich

isotherm, indicated by a higher correlation coefficient (R^2). From Table 5 it can also be seen that the adsorption of CV with M-ZIF-8 has a higher q_e than with ZIF-8 without NaOH. The

6 pseudo-first-order and pseudo-second-order equations are

utilized to represent the adsorption kinetic of CV onto M-ZIF-8 and ZIF-8. The differential form of the

20 pseudo-first-order model is as

follows: $ddqt = k_1(q_e - qt)$ (6) Integration of equation (6) resulting

36 non-linear form of the pseudo-first-order

as follows: $qt = q_e(1 - \exp(-k_1t))$ (7) While the differential form of pseudo-second-order

20 is written as follows $dqt = k_1(q_e - qt)^2 dt$

(8) Integration of equation (8) produces the following equation Fig. 8. (a) Isotherm and (b) Kinetic adsorption plot data of M-ZIF-8 and ZIF-8.

1 Table 5 Langmuir and Freundlich parameters for the CV adsorption onto M-ZIF-8 and

ZIF-8. Langmuir Freundlich Parameters

3 M-ZIF-8 ZIF-8 Parameters M-ZIF-8 ZIF-8

q_m (mg/g) 835.15 556.88 290.61 191.40 (mg/L) $^{-n}$ K_F (mg/g) K_L (L/mg) 0.2331 0.1139 n 4.3556 5.3690 R^2 0.9835 0.9868 R^2 0.8896 0.8868 $qt = q_e \frac{k_1 C}{1 + k_1 C}$ (9) Where qt and q_e

1 are the amounts of dye adsorbed by the solid at any time t and equilibrium condition, the parameters k_1 and

k_2 can be assumed as the time constant

24 for pseudo-first-order and pseudo-second-order, respectively

. Fig. 8(b) shows that the system reached equilibrium in approximately 360 min. The parameters of Eqs. (6) and (7) obtained

20 from the fitting of the experimental data are given in Table

6. According to the values of R^2 , both equations could describe the kinetics adsorption of CV onto

31 M-ZIF-8 and ZIF-8 equally well. The consistency of

the parameter values is critical to determine the model's suitability to represent the adsorption kinetic data. As mentioned before, the parameters k_1 and k_2 are time constant, indicating how fast the equilibrium condition of the adsorption system can be reached. Rapid equilibrium conditions can be indicated by high values of the parameters k_1 and k_2 . The consistency of the values of parameters k_1 and k_2 with experiment kinetic data (Table 6) indicates the model's suitability to represent the adsorption kinetic of the system. As in the adsorption isotherm model, the parameter q_e represents the amount adsorbed at equilibrium condition. The parameter q_e

1 **obtained from the fitting of the experimental data** should close to **the**

value obtained from the experiment. Fig. 8(b) shows that the values of parameter q_e from the pseudo-first-order are close to the experimental data than the pseudo-second-order model (Table 6), indicating the

24 **validity of this model to** represent **the adsorption** kinetic **of**

CV onto M- ZIF- 8 and ZIF- 8. 4.3. Effect of variables on dye photodegradation 4.3.

351. **Effect of pH on CV degradation** The ability **of the**

M- ZIF- 8@TiO₂ composite to degrade organic compounds can be adjusted by varying the pH of the solution. The adsorption ability of the composite also influences the ability of the M- ZIF- 8@TiO₂ to degrade organic compounds. In the case of degradation of some dyes such as

35 **CV, the effect of pH on the degradation**

efficiency is quite challenging to evaluate because the pH of the solution has multiple roles; pH affects the adsorption and degradation ability of the composite. By adjusting the solution pH, the deionization state of surface M- ZIF- 8@TiO₂ can be varied, leading to the alteration of composite adsorption capacity. The availability of the hydroxyl radicals (OH^{*}), which act as the oxidizing agent in the photodegradation process, is also strongly influenced by the solution pH. Hydroxyl radicals are available in excess amounts only at alkaline conditions, between the reaction of positive holes (h⁺) and hydroxyl ions (OH⁻), responsible for enhancing photocatalytic degradation rate. Hydroxyl ions are major species at neutral to high pH values, while positive holes are the major moieties at low pH. Since pH plays a crucial role in evaluating the CV photodegradation efficiency, the photocatalytic behavior of ZIF-8@TiO₂ was evaluated over a broad pH range from 4 to 12 (Jing et al., 2014). At the same time, the color of the CV dye depends on the acidity or alkalinity of the solution. At a strongly acidic solution (<pH = 1.0), the CV color is yellow, while above pH 10 the CV color turns blue. The inconsistent colors are the result of the different charged states of the CV molecules (Adams and Rosenstbin, 1914). Fig. 9(a) depicted that adsorption in higher alkaline solution gives better dye removal in M- ZIF- 8. Fig. 9(b)

9 **shows the** increased **efficiency of CV adsorption/degradation with** increased solution **pH**

. As mentioned earlier, the zero-point charge of M- ZIF- 8@TiO₂ was found in pH 7.8, as seen in Fig. 9(c). Above the pH_{pzc}, the M- ZIF- 8@TiO₂ surface was negatively charged owing to the adsorbed OH ions,

while a positive charge was observed below the pH_{pzc}. Since – crystal violet is a cationic dye, a strong interaction between negatively surface charged of M– ZIF– 8@TiO₂ with the cationic CV became stronger, leading to an increase in the adsorption of CV on composite. At the same time, the presence of excess OH* at high pH accelerated the photocatalytic activity resulting in the reduction of CV due to Table 6

5 Pseudo-first-order and second-order parameters for the adsorption of

CV using ZIF-8. Adsorbent

22 Pseudo first order Pseudo second order k_1 (min⁻¹) q_e (mg/g) R^2 k_2 (g/mg min⁻¹) q_e (mg/g) R^2

M– ZIF– 8 0.0063 93.5229 0.9853 0.0001 107,1561 0.9627 M– ZIF– 8@TiO₂ 5% 0.0044 81.2559 0.9914 0.0001 94.7730 0.9677 Fig. 9. Effect of various aspect on adsorption and photocatalytic dye degradation on M– ZIF– 8; (a)

17 Effect of pH on the adsorption of CV on M– ZIF– 8

; (b)

36 Effect of pH on CV adsorption and photodegradation using

M– ZIF– 8@TiO₂ 5%; (c) pH_{pzc} of M– ZIF– 8@TiO₂ 5%; (d) Effect of mass ratio of TiO₂ incorporated to

3 ZIF-8 and M_ZIF-8 on CV adsorption and photodegradation using M– ZIF– 8

@TiO₂ 5. photocatalytic degradation. 4.3.2. Effect of TiO₂ in

2 M– ZIF– 8 The porosity of M– ZIF– 8

@TiO₂ would help refine mass transfer efficiency and ease the accessibility of active sites for photocatalytic degradation. This phenomenon was studied by varying the mass ratio of TiO₂ (5%, 15%, 25%) incorporated into M– ZIF– 8 (denoted as M– ZIF– 8@TiO₂ X%; X refers to the mass ratio of incorporated TiO₂). Appropriate composition of TiO₂ in M– ZIF– 8@TiO₂ could improve the photoreactivity of the composite. The increase of photoreactivity due to

15 increasing the specific surface area and promoting charge transfer (Du et al)

, 2021). Fig. 9(d) shows the influence of TiO₂ content in M– ZIF– 8@TiO₂ on the degradation of CV. Fig. 9(d) clearly shows that M– ZIF– 8@TiO₂ 5% gave the best performance on the degradation of CV. The result indicates that excessive TiO₂ content results in catalysts aggregation, leading to fewer active sites for photodegradation, reducing light penetration, and leading to light scattering (Du et al., 2021). 4.3.3. Effect of

different coexisting Foreign Ions in Aquatic system In water, the CV solutions coexist with other ions. To explore the competitive effects of various coexisting ions, such as Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , Al^{3+} on CV removal, the optimal conditions were used to conduct the photodegradation experiments. 10 ml of 200 mg/L CV solutions at pH ~9 containing various amounts of NaCl, Na_2SO_4 , KCl, CaCl_2 , and AlCl_3 were prepared. Then, 10

14mg of the **M- ZIF- 8/ M- ZIF- 8@TiO2** was added

into the Erlenmeyer with the prepared solution and shaken for 24 h (6 h in the dark and 18 h under UV light irradiation). After the removal reached equilibrium, the sample and the adsorbent were centrifuged for 10 min at 4900 rpm. Finally, the concentration of CV was tested

by **UV-Visible Spectrophotometer (UV mini 1240 Shimadzu)** at 590 nm. The

addition ions could compete for the adsorptive sites of

3M- ZIF- 8 and M- ZIF 8@TiO2 with CV. Notably, the

negative impact of coexisting ions on CV adsorption and degradation followed the order: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{SO}_4^{2-}$ and Cl^- (Table 7). – especially aluminum. However, the anions, SO_4^{2-} and Cl^- showed A drastic removal rate was observed with the addition of cations, – almost no effect on the adsorption and degradation of CV due to the efficient synergistic effects of dye adsorption and photodegradation using **M- ZIF- 8/M- ZIF- 8@TiO2**. 4.4. Plausible mechanism of photocatalytic degradation of CV on **M- ZIF- 8@TiO2** Photo-induced hydroxyl radicals (OH^*), superoxide anion radicals (

13O_2^{*-}), and holes (**h^+**) are all considered **active species in the**

photo- + catalytic degradation. The free radical scavenging experiments were conducted to discover the major reactive species of **M- ZIF- 8@TiO2** composite during the photodegradation of CV. 1.0 mM isopropanol (IPA), 1.0 mM benzoquinone (BQ),

331.0 mM ammonium oxalate (AO

), and 1.0 mM of sodium azide (SA) were employed as scavengers for OH^* , Table 7 Effect of Different Coexisting Foreign Ions in Aquatic System. Substance Ion Co (mmol/L) Adsorbent %Removal NaCl Cl^- Na_2SO_4 SO_4^{2-} NaCl Na^+ KCl K^+ CaCl_2 Ca^{2+} AlCl_3 Al^{3+} 100

3M- ZIF- 8 M- ZIF- 8@TiO2 5% 100 M- ZIF- 8 M- ZIF- 8

@TiO2 5% 15

3M- ZIF- 8 M- ZIF- 8@TiO2 5% 15 M- ZIF- 8 M- ZIF- 8

3M- ZIF- 8 M- ZIF- 8@TiO2 5% 15 M- ZIF- 8 M- ZIF- 8

@TiO2 5% 97.12 99.32 98.81 99.48 90.33 91.86 90.70 90.93 78.39 84.13 32.53 51.40 O₂^{*-}, h⁺, and 1O₂, respectively. As depicted in Fig. 10(a), CV degradation was evaluated dramatically and moderately obstructed by the presence of BQ and IPA, while insignificantly inhibited by the addition of AO and SA. The following sequence was determined based on the influence of the scavenger on the removal rate: BQ IPA > AO > SA > > No scavenger. In a nutshell, it is evidently proven that O₂^{*-} is the crucial active species in the mechanism of CV. Moreover, employing a 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) quencher, ESR spectroscopic studies were performed to confirm the production of reactive oxygen species O₂^{*-} and OH^{*}. No signal corresponding to the O₂^{*-} and OH^{*} radicals were detected in the dark, as shown in Fig. 10(b). In the presence of UV irradiation, however, the signals for the four typical peaks of DMPO-O₂^{*-} (Jiang et al., 2015; Jin et al., 2021) and quartet pattern (1:2:2:1) of DMPO-OH^{*} were visible (Jin et al., 2021; Chou et al., 2021; Siao et al., 2019), and their intensity rose sharply with increased reaction time. This occurrence suggests

13that O₂^{*-} and OH^{*} as the main active species

has emerged. Fig. 10(c) exhibits the plausible mechanism of M- ZIF- 8@TiO₂ composite throughout the photodegradation system based on the result discussed previously. Regarding the UV-DRS spectrum, the electron excitation of TiO₂ and M- ZIF- 8 during the UV-irradiation (~360 nm) was limited due to a wide bandgap (3.33 and 5.14 eV, respectively). Meanwhile, the composite fabrication of M- ZIF- 8@TiO₂ (5%) narrows the bandgap value (2.97 eV), facilitating the electron excitation and electron/hole pairs creation. The charge migration between MOF and semiconductors was observed, which remarkably limited the recombination of electron/hole. Through UV-light irradiation, the highest occupied molecular orbital (HOMO) of ZIF-8 initially transfers the electron towards the

10lowest unoccupied molecular orbital (LUMO) in ZIF-8

. According to the previous characterization,

26the conduction band of TiO₂ is less negative than the

HOMO potential in ZIF-8. Therefore, the

26conduction band of TiO₂ received the photogenerated

electrons (e⁻) - from M- ZIF- 8

26conduction band while the valence band of TiO₂ transferred the

holes to the M- ZIF- 8 valence band. This phenomenon was significantly effective for photo-generated electron/hole pairs separation to boost photocatalytic activity. Eventually, the dissolved oxygen molecules,

H₂O and OH substances, imprison the excited electron (e⁻) and holes (h⁺) in CB and VB, respectively. The plausible reaction mechanism was presented as follows (Liu et al., 2018; Dong et al., 2015; Chandra and Nath, 2017): $\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e^- + h^+)$ (10) $\text{ZIF-8} + h\nu \rightarrow \text{ZIF-8}(e^- + h^+)$ (11) $\text{TiO}_2(e^-) + \text{O}_2 \rightarrow \text{O}_2^{\cdot-} + \text{TiO}_2$ (12) $\text{ZIF-8}(h^+) + \text{H}_2\text{O}/\text{OH}^- \rightarrow \text{OH}^{\cdot} + \text{ZIF-8}$ (13) $\text{OH}^{\cdot}/\text{O}_2^{\cdot-} + \text{R-H} \rightarrow \text{R}^{\cdot} + \text{H}_2\text{O}/\text{O}_2^{\cdot-}$ (14) According to the trapping experiment result, O₂^{•-} are the major oxidant species in the CV degradation throughout the entire photo-catalytic system.

13The superoxide anion (O₂^{•-}) and hydroxyl radicals (OH[•]) were generated after the

transmission of photogenerated electrons toward oxygen molecules (O₂) and h⁺ on the surface of TiO₂. Subsequently, the catalyst produced OH[•] and O₂^{•-} would benefit adsorbed CV mineralization through oxidation and decomposition on the photocatalyst surface. Meanwhile, the

34high specific surface and mesoporous structure of ZIF-8

particles also positively affect the photocatalytic degradation system of the composites. In common, there are three possible ways of ZIF-8 capture mechanism towards organic pollutants: (1). Open metal sites binding; (2). Electrostatic Interaction; (3). Functional groups interactions between organic pollutants and ZIF-8 (Kong et al., 2017). Therefore, it can be inferred that the integration of TiO₂ with the mesoporous structure of M-ZIF-8 provides excellent merits through a combination of the outstanding adsorption of MOF and photocatalytic advantage from TiO₂ equipped with electron/hole recombine limitation. 4.5.

14M-ZIF-8 And M-ZIF-8@TiO₂ 5% reusability The

15stability of the composite is also a vital factor in the commercial application of the material

for contaminant degradation. The four-cycle experiment and XRD characterization was utilized to study the stability of the composites. The exhausted ZIF-8@TiO₂ was regenerated by three consecutive washing with water and ethanol and re-utilized for several photocatalytic degradations. Fig. 11 depicts the result of CV degradation over M-ZIF-8@TiO₂ (5%) throughout four cycles under UV-light irradiation. At present, the composite maintains its photocatalytic activity during four consecutive cycles. Meanwhile, the XRD after the fourth cycle reveals no insignificant structure deterioration during the photocatalytic reaction based on the peak appearance, as seen in Fig. 11(c). However, it was considerably found intensity reduction at a few peaks of M-ZIF-8@TiO₂, which indicates the adsorption slightly collapses the crystallinity of the composite. In this case, these findings exhibit catalytic activity, and the durability of the manufactured catalyst can be maintained throughout time. The slight reduction acquired during reaction might cause by the pore obstruction and weight during the washing process. Table 8. compares the photocatalytic performance of the as-synthesized catalyst in this work (M-ZIF-8@TiO₂ 5%) with the several published TiO₂-based composite for dye elimination. The comparison is based on the adsorption and photodegradation ability. As presented, our study acquired a much greater capability of adsorption and photodegradation of CV than other published works. In which, this study disclosed the presence of mesoporous structure in ZIF-8 and the TiO₂ ability as Fig. 10. (a). Effect of Quencher Reagent on the Photocatalytic Performance (

33b). DMPO spin-trapping EPR spectra for DMPO-O2 and DMPO-OH

* (c). Mechanism of – photocatalytic degradation of CV on M- ZIF- 8@TiO2. Fig. 11. (a) Cycle experiments of degradation of CV using

3M- ZIF- 8 and (b) M- ZIF- 8@TiO2 5%; (c) XRD Performance of

M- ZIF- 8@TiO2 5% After Several Cycle Experiments. Table 8 Conspectus study of several composites based TiO2 ability for CV photocatalytic adsorption and degradation. Catalyst CV Dosage (mg/L) Reaction Parameter Catalyst pH Dark Reaction Illumination Light Adsorption Conversion (%) Degradation Conversion (%) Ref. Dosage (g/L) Time (min) Time (min) Source MIL-101@TiO2 F-TiO2(B)/fullerene Titanate Nanotube (TNT) T-WOAC TiO2/CP SCA-3 10-Zr-TiO2-600 Graphene-TiO2 M- ZIF- 8 M- ZIF- 8@TiO2 5% 20 5.5 30 0.1 20 3 10 0.4 10 0.2 4,079.8 5 100 0.05 200 1 200 1 n. 40 d. n. 30 d. 6.8 120 9 30 6 30 ~7 1,440 6.5 15 9 360 9 300 40 UV 120 vis 240 UV 120 UV 120 UV 1,320 UV 20 UV 1,080 UV 1,140 UV 51 48 77.23 80 15 31.77 67.24 46 49 78 81.35 16.25 92.30 7.3 (Chang

15et al., 2018) (Panahian et al., 2018) (Mohanty et al., 2020) (Gao et al., 2019) (Ullah et al., 2020) (Vasic et al., 2016) (Shende et al

., 2018) This study This study photocatalytic catalyst act as perfect merits with higher removal activity. 5. Conclusion A hierarchical porous of M- ZIF- 8 has been successfully synthesized in an aqueous solution. By adding NaOH, macro-/mesoporous structures were acquired, still maintaining the mesoporous structure after the TiO2 immobilization. The simultaneous

1adsorption and photocatalytic degradation were conducted in two different conditions. The

1adsorption experiments were conducted in the dark

condition. After

9an equilibrium point was achieved, the suspension was photo-irradiated under UV

light at 360 nm. M- ZIF- 8@TiO2 5% at pH 9 gave the best CV removal efficiency. After four consecutive experiments, M- ZIF- 8@TiO2 shows good performance and stability. The result of this study indicates that titanium dioxide embedded in ZIF-8 composite has excellent potential

9for removal of Crystal Violet from aqueous

solution. CRediT authorship contribution statement Stefanny Angela: Investigation, Methodology, Visualization, Writing – original draft. Valentino Bervia Lunardi: Investigation, Methodology, Visualization,

Writing – original draft. Karissa Kusuma: Investigation, Methodology. Felycia Edi Soetaredjo: Resources, Funding acquisition, Supervision. Jindrayani Nyoo Putro: Validation, Writing – review & editing. Shella Permatasari Santoso: Validation, Writing – review & editing. Artik Elisa Angkawijaya: Resources. Jenni Lie: Investigation, Formal analysis. Chintya Gunarto:

5 Investigation, Formal analysis. Alfin Kurniawan: Formal analysis

, Investigation. Suryadi Ismadji: Conceptualization, Resources, Funding acquisition, Supervision, Writing – review & editing.

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