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2018

Bao, Y., Lim, T.-T., Goei, R., Zhong, Z., Wang, R., & Hu, X. (2018). One-step construction of heterostructured metal-organics@Bi₂O₃ with improved photoinduced charge transfer and enhanced activity in photocatalytic degradation of sulfamethoxazole under solar light irradiation. *Chemosphere*, 205, 396-403. doi:10.1016/j.chemosphere.2018.04.031

<https://hdl.handle.net/10356/139895>

<https://doi.org/10.1016/j.chemosphere.2018.04.031>

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One-step construction of heterostructured metal-organics@Bi₂O₃ with improved
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Abstract

A facile one-step assembly method was developed for the preparation of metal-organics @Bi₂O₃ composites for photocatalysis. Two kinds of metal-organics (Ti-bdc and Cu-btc) @Bi₂O₃ composites were synthesized via the coordination of btc³⁻/bdc²⁻ and metal ions (Ti⁴⁺/Cu²⁺) as well as -OH on the surface of Bi₂O₃. Compared with pure Bi₂O₃, Ti-bdc@Bi₂O₃ shows a 1.7 times higher photocatalytic activity in the degradation of sulfamethoxazole (SMX) under a simulated solar irradiation with a cumulative removal of 62% within 60 min. The high photocatalytic activity could be attributed to the high charge separation, enhanced electron transfer as well as the low recombination rate of photo-generated electrons and holes due to the construction of hetero-structures. The stability test showed that Ti-bdc@Bi₂O₃ is more stable in water than Cu-btc@Bi₂O₃. Furthermore, through the radical-trapping experiments and main intermediates detection, it is demonstrated that the photo-generated holes as well as the •OH and •O₂⁻ formed dominate the photocatalytic decomposition of SMX. These findings demonstrate the potential usage of a facile method to synthesize metal-organics and metal oxides composites, some of which possess high water stability and thus could be employed for water treatment.

Keywords: Metal-organics; Composite; Sulfamethoxazole; Photocatalytic degradation; Charge transfer

1. Introduction

In view of worldwide energy crisis, solar photocatalysis has been recognized as one of the most promising strategies to eliminate organic pollutants in the wastewater owing to the unlimited and sustainable energy influx from the Sun (Kisch, 2013). As one of the typical photocatalyst, TiO_2 has been widely studied. However, because of its wide band gap (~ 3.2 eV) TiO_2 can only be activated by UV irradiation. To address this limitation and better utilize the solar light spectrum, lots of studies have focused on the modification of TiO_2 (Xiang et al., 2017; Zhang et al., 2017a, 2017b, 2015; Zhao et al., 2017) or seek other substitutable materials (Fan et al., 2017; Song et al., 2017). In the substitutable materials, Bi_2O_3 has been extensively studied because of its narrow band gap (*ca.* 2.58~2.85 eV) which corresponds well with the visible spectral range of solar irradiation (Muruganandham et al., 2012; Qin et al., 2014, p.; Wang et al., 2013). Meanwhile, the strong oxidizing ability of Bi_2O_3 also makes it an attractive photocatalyst candidate for wastewater treatment through the direct generation of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ (Zhao et al., 2009a, 2009b). Yet the photocatalytic performance of pure Bi_2O_3 is not optimized due to the poor adsorption of reactants, mass transfer limitation and fast recombination rate of photo-generated electron-hole pairs (Fox and Dulay, 1993). An opportunity to promote the photocatalytic efficacy of catalysts lies in an efficient strategy of constructing a hetero-structured interface with a higher surface area in which photo-electrons could transfer more efficiently at the interface (Fan et al., 2012; Wang et al., 2015, 2016). To achieve this goal, a plausible solution could be integrating Bi_2O_3 with metal-organics which show high surface areas as well as high flexibility.

Metal-organics could be constructed from metal clusters interconnected by terminal organic linkers (Zhou et al., 2012). This kind of material could be employed as an active structure for effective light absorption (C.-K. Lin et al., 2012; Silva et al., 2010; Wang et al., 2011), although the relatively fast recombination rate of photo-generated electron and hole

pairs was still reported (Zhang et al., 2014). Many metal-organics composites have been used for photocatalysis process (Sha and Wu, 2015; Wu et al., 2017; Yang et al., 2015) and the studies on semiconductor metal oxides and metal-organics composites have proven that photo-excited electrons can be effectively transferred from the metal oxide to metal-organics (Abedi and Morsali, 2014; Buso et al., 2012; Esken et al., 2011; Jin et al., 2013; Li et al., 2014; Shen et al., 2013). However, the primary method to synthesize the composites is to load the metal oxides or the metal oxide precursors into the cavities of metal-organics (Hermes et al., 2006; Lu et al., 2012), which is only suitable for particles with small sizes. In a recent study, Bi_2O_3 nanoparticles were successfully encapsulated in the pores of the metal-organics structure and the hetero-structures exhibit superior photo-efficiencies in photocatalytic degradation of nuclear fast red (Guo et al., 2016). In that work, metal organic structures were employed to function as the template to control the synthesis of Bi_2O_3 nanoparticles. Meanwhile, electrodeposition has been used to deposit metal nanoparticles on the substrate (Wang et al., 2017), however, the research on metal-organics@ Bi_2O_3 composites, especially the assembly of metal-organics on the surface of metal oxides is limited.

Herein, we demonstrate a facile one step self-assembly method to synthesize metal-organics@ Bi_2O_3 composites, in which “@” means on the Bi_2O_3 surface in this study. To the best of our knowledge, this is the first report on synthesis of metal-organics@ Bi_2O_3 composite by this method. In this study, two types of metal-organics (Ti-bdc and Cu-btc)@ Bi_2O_3 were synthesized and characterized. The structures, morphologies, optical and electronic properties of composites were investigated. Furthermore, the photocatalytic activity of the resulting composites was investigated via degradation of sulfamethoxazole (SMX) under simulated solar light irradiation.

2. Experimental

2.1 Chemicals

Bismuth (III) citrate ($C_6H_5BiO_7$), copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), titanium(IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$, TTIP), benzene-1,3,5-tricarboxylic acid (H_3BTC , BTC), benzene-1,4-dicarboxylic acid (H_2BDC , BDC), ethanol (C_2H_6O) and poly (propylene glycol)-block poly (ethylene glycol)-block poly(propylene glycol) (PPG-PEG-PPG, Pluronic[®] P-123, P-123, Mw~5800) were purchased from Sigma-Aldrich Co. Ltd. All the reagents were used as received without further purification. The deionized (DI) water used in experiments was produced by a Milli-Q system (18.2 M Ω .cm at 25°C).

2.2 Preparation of Bi_2O_3 and metal-organics@ Bi_2O_3 composite

Bi_2O_3 sample was prepared by direct calcination of bismuth citrate at 550°C for 4 h. To investigate the thermal decomposition behavior of bismuth citrate, the thermogravimetric analysis (TGA) was performed at temperatures from 100 to 700°C using an SDT-Q600 instrument (TA instrument, USA). The sample was heated at a rate of 10 °C min⁻¹ with the air flow of 100 mL min⁻¹. The calculated weight loss of 58% indicates that $C_6H_5BiO_7$ was changed to Bi_2O_3 during the calcination process (Fig S1).

To prepare metal-organics@ Bi_2O_3 composites, a facile one step self-assembly method was employed, which is illustrated in Fig 1. In a typical preparation, a predetermined amount of Bi_2O_3 was dispersed in ethanol (10% P-123 was added as the surfactant to disperse the metal oxide), followed with addition of H_3BTC/H_2BDC with a predetermined concentration, and after 30 min stirring at 65°C, metal precursor with a predetermined molar ratio (Ti/bdc=1:2 and Cu/btc=3:2) was added. The resulting slurry was further stirred for another 30 min to ensure uniform mixing. The detailed composition of the precursor solutions is listed in Table S1. The samples were labelled as Bi_2O_3 and χ M/Bi, where χ is the ratio of M/Bi and M is Ti or Cu.

Fig 1. Schematic diagram of synthesis of metal-organics@Bi₂O₃ composites

2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a Bruker D8 Advance X-rays diffractometer with a monochromated high intensity Cu-K_α ($\lambda = 1.54 \text{ \AA}$) radiation over a 2θ range of 5-60° at a step size of 0.02° combined with a rotation speed of 15 rpm. Fourier transform infrared (FTIR) spectra were measured on a FTIR/NIR Spectrometer Frontier (Perkin Elmer, USA) in the wavenumber range of 4000 to 400 cm⁻¹ with the interval of 1 cm⁻¹, the total scans of 16 and the resolution of 4 cm⁻¹. To further understand the elemental status as well as chemical compositions of MOF@Bi₂O₃ composites, X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos Axis Supra spectrophotometer (Kratos Analytical Ltd, UK) equipped with a dual anode monochromatic K_α excitation source ($h\nu = 1486.71 \text{ eV}$). All binding energies for elements of interest were corrected against an adventitious carbon C 1s core level at 284.6 eV. All XPS peaks were fitted using Shirley background together with Gaussian-Lorentzian function.

The surface properties and EDX elemental distribution were obtained by field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) equipped with an energy

dispersive X-ray spectroscope (EDX, Oxford Xmax80 LN₂ Free). Prior to the analysis, the samples were coated with platinum using Auto Fine Coater (JEC-300FC, JEOL, Japan) for 60 s at current of 20 mA to eliminate the effect of charge accumulation. The high-resolution transmission electron microscope (HRTEM, JEOL 2010) was used to characterize the microstructures of the composites. The Brunauer-Emmett-Teller specific surface areas (S_{BET}) of the as-prepared catalysts were calculated based on BET model from the N₂ adsorption-desorption isotherms obtained at 77 K (Quantachrome Autosorb -1 Analyzer, USA).

2.4 Optical activity evaluation and analyses

UV-vis diffuse reflectance spectra (DRS) of as-prepared samples were recorded on a UV/Vis/NIR Spectrometer (Lambda 950, Perkin Elmer, USA) within the wavelength range of 250 to 800 nm at the data interval of 1 nm. The photoluminescence spectra (PL) were obtained using a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, USA) with the excitation wavelength of 260 nm. Photocurrent studies were measured by an electrochemical workstation (CHI852C) in a conventional three electrode system with Pt wire as a counter electrode and Ag/AgCl as the reference electrode. The working electrode was prepared as follows: 10 mg of the as-prepared catalyst was dispersed into 0.5 mL ethanol and 0.5 mL nafion (0.05%) solution to make homogeneous slurry. The slurry was spread over the FTO glass substrate followed by drying at room temperature. The Na₂SO₄ (0.5 M) aqueous solution was used as electrolyte solution and the full spectrum xenon lamp served as light source. Photocatalytic properties of as-prepared samples were evaluated by degrading target pollutant SMX under simulated sunlight irradiation. The reaction mixture of 10 mg L⁻¹ SMX containing 1 g L⁻¹ catalysts was irradiated with a solar simulator of 300 W supplied by Newport under continuous magnetic stirring. The control experiment was conducted under the same situation but without catalysts. Before the photochemical reactions, all solutions were put in dark for 20 min to achieve the adsorption-desorption equilibrium. The concentration of SMX was

determined using a high-performance liquid chromatography system (LC-2030C 3D, Shimadzu) equipped with a C-18 column. The mobile phases were methanol and 0.1% acetic acid water (v/v, 60/40) at a flow rate of 0.8 mL min⁻¹. The UV detector was operated at a wavelength of 264 nm and the injection volume is 10 µL. The standard curve of SMX detected by the HPLC is shown in Fig S2. The intermediates were further analyzed using an Agilent 1290 Infinity HPLC coupled to an Agilent 6460 Triple quadrupole mass spectrometry, which was equipped with an Electrospray ionization (ESI) source using Agilent Jet Stream Technology (Agilent, USA). The mobile phases consisted of water with 0.1% formic acid and acetonitrile with 0.1% formic acid, which the separations were performed using a 75 mm × 2 mm Luna 3µ C18 column.

3. Results and discussion

3.1 Chemical structure characterization

Powdered-XRD studies were carried out to analyze the phase composition of the composites (Fig 2a). For Ti-bdc@Bi₂O₃ and Cu-btc@Bi₂O₃, the occurrence of Bi₂O₃ peaks in composites is identical to that of pure Bi₂O₃, which indicates that the structural integrity of Bi₂O₃ was not affected obviously by incorporation of Cu-btc and Ti-bdc in the synthesis process. The extra peaks in composites could be attributed to the Cu-btc and Ti-bdc structures compared with the pure Cu-btc and Ti-bdc structures (Fig S3). To further investigate the effect of the metal/Bi ratio, the samples with different ratios of Cu/Bi from 0-2 were examined, and the measured XRD results are shown in Fig S4. The main peaks at 25.8°, 27.1°, 27.6°, 28.2°, 33.5° and 46.2° correspond to (002), (111), (120), (012), (200) and (221) of the monoclinic α-Bi₂O₃ (PDF 04-003-2034).

Fig 2. XRD pattern (a) and FTIR spectra (b) of pure Bi_2O_3 and metal-organics@ Bi_2O_3 composites

Further confirmation of the structural integrity of metal-organics@ Bi_2O_3 is provided by the FTIR spectra presented in Fig 2b. For pure Bi_2O_3 , the bands observed at 431 and 507 cm^{-1} are attributed to stretching vibrations of Bi-O bonds in distorted BiO_6 coordination polyhedron in monoclinic Bi_2O_3 crystals (Ai et al., 2011; Mallahi et al., 2014; Trivedi, 2015). All the Bi-O characteristics peaks were observed in metal-organics@ Bi_2O_3 composites. The presence of organic ligands (BTC/BDC) is evidenced by the strong absorption bands at 1700-1350 cm^{-1} , which can be assigned to the symmetric (1384 and 1405 cm^{-1}) and asymmetric (1650 cm^{-1}) stretching vibrations of carboxylate group, respectively (Classen et al., 2007; Seo et al., 2009, p. 2). These peaks also confirmed the deprotonation of -COOH groups in organic linkers upon the reaction with metal ions (Nguyen et al., 2012; Yang et al., 2016). Additionally, the band at around 730 cm^{-1} and the weak one at 1110 cm^{-1} are attributed to metal-O bond (Lin et al., 2014) and C-O-metal stretching (Hu et al., 2010), respectively. The spectra of pure Cu-btc and Ti-bdc is presented in Fig S5. Meanwhile, the effect of metal/Bi ratio was also examined (Fig S6), showing both metal-organics and Bi_2O_3 structures were preserved in the metal-organics@ Bi_2O_3 composites.

The chemical compositions and electronic structures of metal-organics@ Bi_2O_3 were analyzed by XPS spectroscopy. Fig S7 shows the high-resolution spectra of Ti 2p and Cu 2p,

which indicates the presence of Ti and Cu in metal-organics@Bi₂O₃ composites. The survey spectra of metal-organics@Bi₂O₃ composites as well as high-resolution XPS spectra of the Bi 4f regions are shown in Fig 3. The peak of Bi 4f_{7/2} in Bi₂O₃ shows the binding energy of 160.5 eV (Nefedov et al., 1975; zhong Zhao and biao Zhang, 1994) and the peak with binding energy of around 165.8 eV is identified as Bi 4f_{5/2} in Bi₂O₃ (Afsin and Roberts, 1994), both of the peaks can be assigned to a Bi³⁺ oxidation state. Additional weak spin-orbit doublet peaks for Bi 4f_{7/2} (158.4 eV) and Bi 4f_{5/2} (163.8 eV) are also detected, suggesting that some of Bi exist as multiple valence states, which could be attributed to the substoichiometric phase in the sample (Wu et al., 2008). Compared to the pure Bi₂O₃, the obvious binding energy drifts in metal-organics@Bi₂O₃ composites should be caused by the formation of the metal-organics-Bi₂O₃ heterojunction. The interfacial interactions could affect the electronic structures of composites, which should impact their catalytic properties. For Cu-btc@Bi₂O₃, the disappearance of multiple valence states might be unfavorable for electrons transition.

Fig 3. XPS spectra of wide scan (a) and high resolution of Bi 4f in Bi₂O₃ (b), 1 Ti/Bi (c) and 1 Cu/Bi (d)

3.2 Physical properties characterization

The morphology of as-prepared composites was analyzed by FESEM, which shows they are composed of Bi_2O_3 particles and clusters containing metal-organics with an average size of around 200 nm (Figs 4 c and e). In the synthesis process, the organic linkers ($\text{btc}^{3-}/\text{bdc}^{2-}$) were first grafted on the Bi_2O_3 surface via the covalent interaction between the carboxyl groups on BTC/BDC and the hydroxyl groups on the oxides (Bertazzo and Rezwan, 2010). The residual carboxyl groups on BTC/BDC then bonded with metal precursors during the next deposition (Fig 1). The EDX elemental mappings (Figs 4 d and f) show that Ti and Cu are homogeneously distributed on the surface of as-prepared composites. The composites with hierarchical structure containing micro, sub-micro and nano-scale elements may result in a higher photocatalytic activity (Zhao et al., 2006). With the increasing of the metal/Bi ratio in the composites, more metal-organics particles were deposited on the Bi_2O_3 surface (Fig S8). Since metal-organics and Bi_2O_3 were intimately contacted, an ohmic layer was likely formed between them, which would facilitate inter-particle electron transfer. Meanwhile, the hierarchical structure in composites would also result in higher surface areas compared with the pure Bi_2O_3 (Fig S9), which is favorable for the pollutant adsorption in the photocatalysis process.

The microstructure of 1 Ti/Bi was further examined by HRTEM, which is shown in Fig S10. For this sample, the MOF layer was approximately 20 nm thick and featured randomly oriented nanocrystals on the surface of Bi_2O_3 . While, the Bi_2O_3 had the form of highly crystalline elongated platelets. The similar structure was also found in the 1Cu/Bi sample, which shows the hetero-interface between Bi_2O_3 and metal-organics. This hetero-structure could form some defective interface, which would enhance the electron transfer, improving the photocatalysis efficiency.

Fig 4. FESEM images and EDX elemental mappings of pure Bi_2O_3 and metal-organics@ Bi_2O_3 composites

3.3 Optical properties

UV-Vis spectrum was used to study the energy structures and optical response of metal-organics@ Bi_2O_3 composites. The measured diffuse reflectance spectra are shown in Fig 5a, in which the pure Bi_2O_3 has an absorption edge at approximately 440 nm, corresponding to a band gap of around 2.81 eV. The Cu-btc@ Bi_2O_3 composite shows a strong absorption in the range of 550-700 nm due to the photo absorption of Cu-btc (K.-S. Lin et al., 2012), which could be caused by a d-d transition of octahedral Cu(II) ions (Prestipino et al., 2006; Yoon et al., 2010).

The UV-vis spectra absorption bands of composites at about 370 nm are attributed to organic ligand-to-metal charge transfer (LMCT).

Photoluminescence (PL) emission spectra have been widely used to investigate the efficiency of charge carrier trapping and transfer and to understand the fate of electron-hole pairs in semiconductors (Yamashita et al., 1997). The excitation wavelength was set at 260 nm and the emission spectra of Bi_2O_3 and as prepared composites are shown in Fig 5a (Inset). The main emission peak is centered at wavelength of 535-545 nm for all samples. The PL emission intensity decreases with incorporation of Ti-bdc and Cu-btc due to the inhibition of electron-hole recombination in metal-organics@ Bi_2O_3 composite (Zamaro et al., 2012), which could be conducive to photocatalysis process.

The separation of photogenerated electron-hole pairs was evaluated by measuring the photocurrent responses of as prepared materials under simulated solar irradiation. As shown in Fig 5b, the photocurrent density of pure Bi_2O_3 based electrode under light irradiation was recorded as *ca.* $1 \mu\text{A cm}^{-2}$. However, the photocurrent densities of the 1 Ti/Bi and 1 Cu/Bi increased to 6 and $3 \mu\text{A cm}^{-2}$ under the same system, which were approximately 6 times and 3 times higher than that of the pure Bi_2O_3 , respectively. Meanwhile, the photocurrent of pure metal-organics is quite low (data not shown), meaning the metal-organics has a limited photocatalytic ability. The enhanced photocurrent of the composites could be ascribed to the decoration of metal-organics onto the Bi_2O_3 surface, resulting in faster electron transport inside the composites and higher separation efficiency of photogenerated electron-hole pairs.

Fig 5. Photo-activity of pure Bi_2O_3 and metal-organics@ Bi_2O_3 composites: a) UV-Vis diffuse reflectance spectra (DRS) and photoluminescence curve (PL, inset); b) Photocurrent responses; c) Plots of C_t/C_0 versus time of SMX degradation under simulated solar irradiation on different catalysts and d) photocatalytic performance evaluation of 1 Ti/Bi and P25 (Initial concentration of SMX, 10 mg L^{-1} ; catalyst loading, 1 g L^{-1} ; irradiation intensity, 1 Sun)

The photocatalytic activity of as-prepared composites was tested for SMX degradation reaction. SMX has been used widely to treat bronchitis and urinary tract infections and the release of SMX has caused environmental pollution as well as human diseases (Trovó et al., 2009; Walker et al., 2013). Fig 5c shows the photocatalytic activities of the as-prepared catalysts in photocatalytic degradation of SMX under simulated solar irradiation. The photocatalytic degradation of SMX follows pseudo-first-order kinetics with reaction rate constants k of 0.007, 0.013 and 0.008 min^{-1} on pure Bi_2O_3 , 1 Ti/Bi and 1 Cu/Bi, respectively.

A total of 62% of SMX at the initial concentration of 10 mg L⁻¹ was degraded in 60 min under the simulated solar irradiation on 1 Ti/Bi composites. The preliminary results show that the higher photocatalytic activity of the metal-organics@Bi₂O₃ composites could be attributed to the formed hierarchical structure with generation of an ohmic contacts as well as the suppression of electron-hole recombination. In the following experiment, the photocatalytic performance of Ti-bdc@Bi₂O₃ was compared with the commercial P25 under visible light irradiation and the results show that the degradation of SMX on P25 under visible light irradiation is negligible (less than 10% in 60 min) (Fig 5d).

Additionally, the aqueous stability of metal-organics@Bi₂O₃ was evaluated. After soaking the as-prepared composites in reaction solution for 3 days, the structure of Ti-bdc@Bi₂O₃ was preserved, while that of Cu-btc@Bi₂O₃ collapsed, indicating that Ti-bdc@Bi₂O₃ had a higher aqueous stability compared with Cu-btc@Bi₂O₃, which could be used for long-term water treatment (Fig S11).

3.4 Photocatalytic degradation mechanism

To further investigate the roles of different reactive oxygen species (ROS) in SMX degradation, four scavengers namely oxalate, dimethyl sulfoxide (DMSO), benzoquinone (BQ) and NaN₃ were added as quenchers of h⁺, •OH, •O₂⁻ and ¹O₂, respectively (Bao et al., 2017). The inhibition effect shows that the •OH and •O₂⁻ were two major radicals generated in this process, and the direct oxidation via photo-generated h⁺ played a vital role as well (Fig 6a). To explore the intermediate products and degradation pathway of SMX, LC/MS/MS was utilized via the ES (+) mode (Fig S12). As shown in Fig 6b, the degradation happens with the cleavage of sulfonamide bond (m/z 99.1 and 158.1). Subsequently, ring opening reactions occurred, which resulted into formation of mineral acids and mineralized products. In the degradation process, it is hypothesized that both metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) happened because of the multi-valence states of bismuth,

resulting a complementary light absorption to the inter-band transitions, enabling broadband light harvesting. When Bi is oxidized to a relatively high valence state and the electro-accepting ligands offer rather stable empty orbitals. In this case, the electrons are excited from an occupied metal-localized orbital to a vacant ligand-localized orbital, resulting in long-wavelength light absorption (MLCT). When Bi is reduced to a relatively low valence state while the electron-donating ligands offer donor orbitals, the electrons can be excited from a ligand donor orbital to the metal center, absorbing low-energy photons (LMCT) (Kalyanasundaram and Grätzel, 2013).

Fig 6. (a) Photocatalytic degradation of SMX on 1Ti/Bi with different scavengers; (b) Main products detected in SMX photocatalytic degradation and (c) Schematic illustration for the metal-to-ligand charge transfer (blue line) and ligand-to-metal charge transfer (red line) in 1Ti/Bi composites (Conditions: initial concentration of SMX, 10 mg L⁻¹; catalyst loading, 1 g L⁻¹; irradiation intensity, 1 Sun, reaction time, 60 min).

As shown in Fig 6c, the growth of metal-organics on the surface of Bi_2O_3 was formed by the chemical coordination. In MLCT, the electrons are excited from the occupied metal localized orbital to a vacant ligand-localized orbital, resulting in long wavelength light absorption. Meanwhile, the existence of bridge ligands in metal-organics makes the distance between photo-generated electrons and holes become spatially sufficient to reduce their recombination (Fig 6c, blue line). In LMCT, the organic ligands in metal-organics can absorb visible light by exciting electrons from the chelating ligand directly into the conduction band of Bi_2O_3 , which renders a red shift to the Bi_2O_3 light absorption and enables efficient solar light harvesting. Meanwhile, the high electron density of aromatic carboxylates in metal-organics favors the electron transfer to the central metal cations upon photo-absorption (Fig 6c, red line). Both electrons and holes can react with H_2O and O_2 to generate some radicals ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$), which can attack SMX molecules.

4. Conclusions

Two types of metal-organics (Ti-bdc and Cu-btc) were successfully anchored onto the surface of Bi_2O_3 by a facile one step method via coordination at low temperature. The composites showed improved photocatalytic activities on the degradation of SMX under a simulated solar irradiation. The rate constants increased from 0.007 min^{-1} for pure Bi_2O_3 to 0.013 min^{-1} and 0.008 min^{-1} for $\text{Ti-bdc@Bi}_2\text{O}_3$ and $\text{Cu-btc@Bi}_2\text{O}_3$, respectively, resulting in the total SMX removal of 43%, 62% and 47% under the same reaction conditions. The higher performance of composites could be attributed the higher surface area as well as heterojunction formation between metal-organics and Bi_2O_3 , which could enhance electron transfer (MLCT and LMCT) and inhibit the recombination of photo-generated electron-hole pairs. Meanwhile, $\text{Ti-bdc@Bi}_2\text{O}_3$ showed a higher stability in water, the structure could be preserved even after soaking in water for 3 days. The photocatalytic degradation of SMX accompanied by the

cleavage of sulfonamide bond, in which both direct oxidation via holes and indirect oxidation via generated $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ played a vital role.

Acknowledgement

The sample characterization (FESEM, HRTEM and XRD) work was performed at the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore. Also, the authors would like to thank Dr. Yen Nan Liang, Mr Heng Yeong Lee and Ms. Yu Shan Tay from Nanyang Technological University for their help in collecting EDX and TEM data.

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