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1. Introduction

Population growth has created ever-growing global issues related to energy demand and availability of clean water. Active research work is being conducted to address these issues. In meeting the energy needs, solar energy has been harnessed and incorporated in existing industrial processes. This would ease the high demand for energy and alleviate the harm caused by traditional power generation to our environment. The scientific community has actively sought photocatalysts that enable the technology to use sunlight to treat contaminants in wastewater.¹⁻⁴ One area, which has been addressed by these studies, is the photoreduction of toxic heavy metal hexavalent chromium Cr(vi) ions to the water-insoluble trivalent form of Cr(III) under light irradiation⁵⁻⁷ by inorganic semiconductor materials or their heterostructures, such as Bi₄O₇, Fe₃O₄, TiO₂ and Bi₂WO₆.⁷⁻¹² During the progress of materials development, a novel photocatalyst was developed based on a layered microstructure of Bi₂WO₆ with a sub-nanosized perovskite $(WO_4)^{2-1}$ layer bridging between $(Bi_2O_2)^{2+}$ layers and this opens up a new strategy to make materials with distinctively advantageous



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A new conductive metal–organic-framework (MOF) photocatalyst, $(WO_4)^{2-}$ -doped bismuth terephthalate (referred to as nNa_2WO_4BiBDC), was synthesized and characterized by varying the precursor molar ratio (n = 0.1, 0.3, 0.4, and 0.5) of $Na_2WO_4/Bi(NO_3)_3$ in the presence of terephthalic acid through a one-pot solvothermal process. This study found that doping $(WO_4)^{2-}$ into BiBDC enhanced the separation of photo-generated carriers, improved the photocatalytic properties of bismuth terephthalate (BiBDC), and enabled the application in Cr(vi) reduction under UV light irradiation with the synergic effect from citric acid acting as a hole scavenger. Among all the precursor ratios of $Na_2WO_4/Bi(NO_3)_3$ used, $0.4Na_2WO_4BiBDC$ has the optimum performance, leading to triple gain in reduction efficiency for undoped BiBDC. The synthetic strategy to dope $(WO_4)^{2-}$ into a layered MOF as a viable option for modification of MOFs was demonstrated in this study. Finally, the photoreduction of Cr(vi) by $(WO_4)^2$ -doped bismuth terephthalate enables a new promising wastewater treatment option.

> characteristics such as good stability, high surface area and most importantly good conductivity. Xu *et al.* reported inorganic semiconductors BiOX (X = Cl, Br, and I) bridging between $(Bi_2O_2)^{2+}$ layers with excellent photocatalytic performance for the reduction of Cr(v1).^{13,14} Hence, $(Bi_2O_2)^{2+}$ -based layered metal organic frameworks have become a new class of material for the development of photocatalysts.

> Metal organic framework materials (MOFs) have been developed into photocatalysts for pollutant removal owing to their large surface area, porous microstructure, variable metal node and organic bridging linker in the past few decades.^{15,16} Combination of metal-organic framework materials with an inorganic semiconductor is considered as the latest strategy to improve photocatalytic performance.^{17,18} In our previous work, (Bi₂O₂)²⁺-based layered bismuth terephthalate (abbreviation as BiBDC) for photocatalysis was well studied for photocatalytic reduction of 4-nitrophenol and organic pollutant RhB removal. These catalysts were formed by doping halogen anions and metal bismuth into BiBDC to improve the photocatalytic performance of bismuth terephthalate.¹⁹⁻²² Similar research work based on bismuth terephthalate for photocatalytic oxidation of organic dyes has been reported, but bismuth terephthalate itself has no activity.^{23,24} But to date, there is no report of photocatalytic reduction of Cr(vi) by bismuth terephthalate and its derivatives so far.

> Bismuth terephthalate displays an interesting layered structure as its $(Bi_2O_2)^{2^+}$ layers are linked by benzene rings ($-C_6H_4-$). Likewise, the $(WO_4)^{2^-}$ layers and the halogen layers bridging



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between the two $(Bi_2O_2)^{2^+}$ layers in Bi_2WO_6 and BiOX inherit the same characteristics but the photoactivity of $(WO_4)^{2^-}$ in bismuth-terephthalate-based MOFs remained unknown before this study.^{25,26} The positively charged $(Bi_2O_2)^{2^+}$ layers in bismuth terephthalate provide an ideal environment for doping negatively charged photoactive species such as $(WO_4)^{2^-}$ and the study of its photoactivity after doping will reveal its role in photoreduction. Herein, different photocatalysts were prepared by controlling the amounts of Na_2WO_4 relative to $Bi(NO_3)_3$ in the presence of terephthalic acid under solvothermal heating. The synergy between $(WO_4)^{2^-}$ and bismuth terephthalate for photocatalytic reduction of $Cr(v_I)$ was investigated from various concentrations of doped $(WO_4)^{2^-}$ in bismuth terephthalate under UV light irradiation. The enhanced photocatalytic reduction was analyzed along with a proposed catalytic mechanism.

2. Experimental section

2.1 Preparation of photocatalysts

2.1.1 Preparation of $(WO_4)^{2-}$ -doped samples. Typically, the amounts of Bi(NO₃)₃·5H₂O (1.33 mmol) and terephthalic acid (2.0 mmol) were kept constant for all different photocatalyst samples, while different amounts of Na2WO4·2H2O as the precursor for $(WO_4)^{2-}$ doping were used to achieve five precursor molar ratios of $Na_2WO_4/Bi(NO_3)_3$ (indicated as n = 0, 0.1, 0.1) 0.3, 0.4, and 0.5) by performing exactly the same experimental procedure. The synthesis started with dissolving $Bi(NO_3)_3 \cdot 5H_2O_3$ (0.645 g, 1.33 mmol), in 20 mL of N,N-dimethylformamide (DMF) by applying ultrasonication for 30 min, while terephthalic acid (0.332 g, 2.0 mmol) was prepared separately by dissolving it in 15 mL of DMF. Then, 0.67 mmol of Na2WO4·2H2O was added into terephthalic acid solution and sonicated for 15 min to make the sample with a precursor molar ratio of 0.5 (labeled as n = 0.5). The Bi(NO₃)₃ solution was then mixed with Na₂WO₄ solution containing terephthalic acid by sonication for 15 min. Finally, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 120 °C for 24 h without stirring. After being cooled to room temperature, the precipitate was filtered, washed thoroughly with ethanol and water, and then dried at 100 °C. From the different precursor molar ratios used in synthesis, five produced solids were labeled as BiBDC, 0.1Na₂WO₄BiBDC, 0.3Na₂WO₄BiBDC, 0.4Na₂WO₄BiBDC, and 0.5Na2WO4BiBDC corresponding to the prepared molar ratios of $Na_2WO_4/Bi(NO_3)_3$ (n = 0, 0.1, 0.3, 0.4, and 0.5), respectively.

2.1.2 Preparation of the terephthalate-free sample. Similar to the process mentioned above, the preparation of the terephthalate-free sample started by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ (0.645 g, 1.33 mmol) in DMF (20 mL) with sonication. In a separate beaker, $Na_2WO_4 \cdot 2H_2O$ (1.33 mmol) was sonicated and dispersed in DMF (15 mL). It was mixed, heated, and dried according to the same procedure described above and labeled as the control.

2.2 Characterization of catalysts

The as-prepared catalysts were characterized by powder X-ray diffraction (XRD) (Bruker D8 Advance; Cu K α = 1.5404 Å).

The surface morphology and chemical composition of the catalyst were observed using a Talos F200X field-emission scanning/transmission electron microscope (STEM, Thermo Fisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using Al Ka radiation as the excitation source under vacuum at 2 \times 10⁻⁶ Pa. All the binding energy (BE) values were calibrated by the C 1s peak at 284.6 eV of the surface adventitious carbon. The contents of W and Bi elements were determined on a NexION-300 inductively coupled plasma-mass spectrometer. UV-vis diffused reflectance spectra (DRS) were measured on a Shimadzu UV-2550 spectrophotometer using BaSO₄ as a reference. Fourier transform infrared (FT-IR) spectra were measured using a Thermo Scientific Nicolet NEXUS 4700 using the KBr disk. The specific surface areas and pore size distribution of the as-prepared samples were determined on an ASAP 2020 type N2 physical adsorption-stripping analyzer by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained from the data in BJH desorption pore distribution. Raman analysis was conducted on a DXR2 xi Raman imaging microscope (Thermo Fisher Scientific, USA) equipped with a 633 nm He-Ne laser source. Transient photocurrent densities, Mott-Schottky and electrochemical impedance spectroscopy (EIS) Nyquist plots of the as-prepared samples were obtained from a CHI760E electrochemical station using an Ag/AgCl electrode as the reference electrode, a platinum electrode as the counter electrode, the as-prepared samples coated on ITO as the working electrode and 0.5 M Na₂SO₄ solution as the electrolyte at frequencies of 1000 and 2000 Hz, respectively. A UV LED light (3 W) was used as the light source with 50 s on-off cycles.

2.3 UV light photoreduction of Cr(vi)

Photoreduction of Cr(vi) was carried out in a 100 mL doublewalled photoreactor, jacketed with circulating water between the two walls at 25 °C with UV light irradiation. The UV light source was a 350 W xenon lamp with a 365 nm cut-off filter. In a typical procedure, 50 mg of the as-prepared catalyst was dispersed in 50 mL of aqueous K₂Cr₂O₇ solution (equivalent to 20 mg $Cr(v_I)/L$) with ultrasonic bath treatment for 10 min. The suspension was stirred for 2 h in the dark to establish the equilibrium of adsorption-desorption. Then the suspension was irradiated with UV light under stirring. 3 mL of the suspension was sequentially removed at specified time intervals and centrifuged (8000 rpm, 10 min) to remove the catalyst. Then the residual concentration of the solution was determined colorimetrically at 540 nm using the diphenylcarbazide (DPC) method.²⁷ Briefly, 1 mL of the photolyzed solution was mixed with 9 mL of 0.2 M H₂SO₄ in a 10 mL plastic centrifuge tube. Subsequently, 0.2 mL of freshly prepared 0.25% (w/v) diphenylcarbazide in acetone was added to the tube. After mixing, it was allowed to stand for about 15 min to ensure full color development. Absorbance of the solution was determined at 540 nm using deionized water as a reference.

3. Results and discussion

3.1 Compositions and microstructures of the as-prepared samples

The synthetic strategy employed in this study is to dope different amounts of $(WO_4)^{2-}$ into layered bismuth terephthalate by a solvothermal method so that their compositions and properties can be compared with the blank bismuth terephthalate and terephthalate-free samples. The prepared molar ratios (*n*) of Na₂WO₄/Bi(NO₃)₃ (*n* = 0, 0.1, 0.3, 0.4 and 0.5; indicated as *n*Na₂WO₄/BiDC) were designed to determine the optimum (WO₄)²⁻ composition for maximum photocatalytic activity of the composite. The powder XRD patterns of the as-prepared samples were investigated and the results can be seen in Fig. 1. The control sample prepared from Na₂WO₄ and Bi(NO₃)₃ has poor crystallinity.

The peaks of 2θ at around 28.5° , 32.8° , 47.0° , and 54.5° closely match with the XRD patterns of Bi₂WO₆ (28.3°, 32.8°, 47.1°, and 55.8°).²⁸ The control sample does not have the benchmark peak of terephthalate at around 5.6° as the control sample is free of terephthalate in its synthesis. For the $(WO_4)^{2-}$ doped samples with the prepared molar ratios of Na₂WO₄/ $Bi(NO_3)_3$ varying from 0.1 to 0.4, the benchmark peak of terephthalate was shown in their XRD patterns, suggesting that the scaffold of bismuth terephthalate was intact. The benchmark peaks in (WO₄)²⁻-doped samples had shifted toward lower angles as shown in Fig. S1 of the ESI,† as the extension of interplanar spacing of the crystal was found when the diffraction angle becomes smaller according to the Bragg's law.²⁹ In addition, a new diffraction peak at 7.5° was observed indicating strong interaction between doped $(WO_4)^{2-}$ and BiBDC. However, both the benchmark peak and peak at 7.5° were not observed in the sample with Na₂WO₄/Bi(NO₃)₃ ratio at 0.5. This can be explained by the coordination of Bi^{3+} with terephthalic acid being disrupted by the excess Na₂WO₄, leading to the disintegration of the scaffold of the metal organic framework.

XPS measurements were performed on $0.4Na_2WO_4BiBDC$ to identify the surface elements within the Na_2WO_4BiBDC



Fig. 1 The powder XRD diffraction patterns of the as-prepared samples.

composite and learn its chemical nature state. The widerange spectra (binding energy locating in the range of 0-800 eV) of 0.4Na₂WO₄BiBDC and BiBDC are displayed in Fig. 2a, which reveal strong signals for C, O, W and Bi elements but no detectable signal from the Na element. The high resolution XPS spectra for Bi 4f, W 4f, O 1s and C 1s are depicted in Fig. 2b-d and Fig. S2 (in the ESI⁺). First, two peaks for Bi 4f were observed at 159.7 eV and 165.1 eV, corresponding to Bi³⁺ states of Bi 4f7/2 and Bi 4f5/2, respectively, comparable to previously reported values.30 Comparing with those of the BiBDC sample (159.3 eV and 164.5 eV), a slight peak shift toward a higher binding energy for Bi³⁺ was observed. This suggests that a strong interaction exists between Bi³⁺ and O atoms from $(WO_4)^{2-}$ leading to an increased binding energy. Secondly, two peaks at 36.0 eV and 38.2 eV for W 4f can be assigned to W $4f_{7/2}$ and W $4f_{5/2}$ and both peaks are higher than the peaks from the reported Na_2WO_4 (35.9 eV and 37.7 eV),³¹ due to the strong interaction between Bi³⁺ and doped O atoms within $(WO_4)^{2-}$. Thirdly, the binding energy of O 1s (530.5 eV) shows a decrease when comparing with that of BiBDC (530.9 eV), another indication for the presence of strong interactions between doped anionic $(WO_4)^{2-}$ and cationic $(Bi_2O_2)^{2+}$ layers within BiBDC. Finally, C 1s shows two peaks at 284.6 eV and 288.4 eV corresponding to aromatic carbons on the benzene ring and the carbons within carboxylate groups as strong evidence for the stable-scaffolded carbon of bismuth terephthalate (Fig. S2 in the ESI[†]).

The chemical structures of the as-prepared samples have been investigated by FT-IR and Raman spectra and their results are shown in Fig. 3, Table 1 and Fig. S3a-e, S4a-e (in the ESI⁺). Major Raman peaks were found in the range of 50–2000 cm^{-1} (Fig. 3a). Bismuth terephthalate shows all the characteristic Raman vibrational peaks at 1609(s), 1505(w), 1409(s), 1133(w), 859(s), 632(w) and 309(s) cm⁻¹ in which the peaks at 1505 and 1409 cm⁻¹ are of great significance as they are the asymmetric and symmetric stretch modes of the coordinated -COOgroups for terephthalate.³² The peak at 309 cm⁻¹ is attributed to the presence of vibrational modes involving Bi³⁺ species.^{33,34} Evidently, all the peaks found in BiBDC are similar to those of previously reported NiBDC (peaks at 1612, 1428, 1136, 871 and 632 cm^{-1} ,³⁵ strongly suggesting the stable complexation between Bi^{3+} and terephthalic acid. After $(WO_4)^{2-}$ was doped into BiBDC, Raman signals from the prepared samples well matched with those of BiBDC, indicating the stable framework of bismuth terephthalate in the doped samples. Interestingly, the intensities of two peaks at 1409 $\rm cm^{-1}~(\nu_{s(\rm COO)})$ and at 309 cm⁻¹ decrease with an increase in the amount of Na₂WO₄ used during synthesis and such an increase reflects the strong interaction between doped (WO₄)²⁻ and BiBDC as doped $(WO_4)^{2-}$ anions affect the symmetrical stretching mode of carboxylate. But this observation was not found in the doped sample, 0.5Na₂WO₄BiBDC. From the FT-IR spectrum of BiBDC (Fig. 3b), the intense peaks at 1382 and 1532 cm^{-1} are attributed to O-C-O the symmetric stretching and the asymmetric stretching within carboxylate as an effective functional group or linker to form a coordination bond with Bi³⁺. All (WO₄)²⁻ doped



Fig. 2 Survey XPS spectra (a). Core level Bi 4f spectra (b). Core level XPS spectrum of W 4f (c), and core level XPS spectra of O 1s (d) within $0.4Na_2WO_4BiBDC$, and BiBDC.



Fig. 3 Raman (a) and FT-IR (b) spectra of the as-prepared samples.

Table 1 Raman and FT-IR data of the as-prepared samples

Samples	Raman bands	IR-characteristic strong peaks of COO ⁻ for the samples
BiBDC	3073, 1609(s), 1505, 1409(s), 1133, 859(m), 632, 309(m), 153, 110, 77(s)	1382, 1532
0.1Na ₂ WO ₄ BiBDC	3070, 1610(s), 1417(s), 1131, 859(s), 634, 314, 152(s)	1382, 1513
0.3Na ₂ WO ₄ BiBDC	3076, 1609(s), 1419, 1129, 860(s), 634, 353, 145(s)	1380, 1512
0.4Na ₂ WO ₄ BiBDC	3080, 1610(s), 1413, 1127, 858, 634, 353, 142, 98, 70(s)	1382, 1508
0.5Na ₂ WO ₄ BiBDC	3087, 1611(s), 1126, 833(s), 633, 353, 265, 105(s), 72(s)	1379, 1526

bismuth terephthalate catalysts show similar vibrational modes in the same vibrational range, which suggests the good coordination of Bi^{3+} with terephthalic acid. The result from $0.5Na_2WO_4BiBDC$ shows only one of two carboxylic groups within terephthalic acid coordinating with Bi^{3+} when $(WO_4)^{2-}$ anions were doped (Table 1, Fig. 3a and Fig. S4a–e, ESI†). This may contribute to its different XRD pattern observed when comparing with other Na_2WO_4BiBDC samples. Two peaks at 1382 and 1532 cm⁻¹ show intensity inversion for nNa_2WO_4 . BiBDC (n = 0.3, 0.4 and 0.5) compared to those of BiBDC, suggesting that doped (WO_4)²⁻ has a strong interaction with O atoms within BiBDC, which leads to increased symmetrical stretching intensity due to IR technology-detection for unsymmetrical stretching modes.

The other aspects of structural characterization were examined by BET specific surface area and pore size distribution through N₂ adsorption–desorption and their results are correlated to the results of ICP-MS shown in Fig. 4 and Table 2. BET specific surface areas for the samples BiBDC, $0.4Na_2WO_4BiBDC$ and $0.5Na_2WO_4BiBDC$ are determined to be 26.81, 15.59 and 29.03 m² g⁻¹, respectively. Combination of pore size distribution and IV type isotherm plot with an H3 hysteresis loop exhibits their unique macropore structure as a stacking-layered microstructure.

The $(WO_4)^{2-}$ doped bismuth terephthalate samples were studied further by the determination of actual W/Bi atomic ratios from ICP-MS analysis. From Table 2, actual atomic W/Bi

 Table 2
 BET specific surface area and actual atomic ratios of W/Bi within the as-prepared samples

Samples	BET surface areas $(m^2 g^{-1})$	Actual atomic ratios of W/Bi
BiBDC	26.81	0
0.1Na ₂ WO ₄ BiBDC	ND	0.11
0.3Na ₂ WO ₄ BiBDC	ND	0.45
0.4Na ₂ WO ₄ BiBDC	15.59	0.35
0.5Na ₂ WO ₄ BiBDC	29.03	0.16
Control	ND	0.27

ND: the corresponding data were not determined.

ratios for the samples $0.1Na_2WO_4BiBDC$ and $0.4Na_2WO_4BiBDC$ are in accordance with the prepared molar ratios. But the actual atomic ratios of W:Bi for other samples are slightly inconsistent possibly due to the complex behavior for Bi³⁺ to combine with the terephthalic acid or $(WO_4)^{2-}$ anions in DMF solution. Moreover, the effects of different doping amounts of $(WO_4)^{2-}$ anions on the coordination degree of Bi³⁺ with terephthalic acid were different.

0.4Na₂WO₄BiBDC was also analyzed by STEM coupled with energy dispersive X-ray spectroscopy (EDX) to confirm the morphology and composition. The high-angle annular dark-field (HAADF) STEM image and its energy-dispersive X-ray elemental mappings can be seen in Fig. 5. Lamellar microstructures can be observed. Carbon, oxygen, bismuth and tungsten elements are uniformly distributed within



Fig. 4 N₂ adsorption-desorption isotherm plots (a) and pore size distribution for the as-prepared samples (b).



Fig. 5 STEM image of 0.4Na₂WO₄BiBDC (a), HAADF STEM image (b) and STEM-energy dispersive X-ray (STEM-EDX) elemental mappings of Bi, W, O, and C (c-f).

 $0.4 Na_2 WO_4 BiBDC.$ SEM images of other lamellar samples can be found in Fig. S6 (in the ESI†).

One effective way to examine the insertion of $(WO_4)^{2^-}$ anions into the internal cavity of bismuth terephthalate is to investigate the crystal structure of bismuth terephthalate with CCDC 793572 using computer modeling.²⁶ From Fig. 6, the values for cell parameters *a* and *c* of bismuth terephthalate are 10.1 and 11.8 Å, respectively. In the (001) facet, the distance of the nearest two benzene rings is 8.0 Å, while the modeled bond length of the W–O bond is 1.78 Å. Considering the tetrahedral configuration of $(WO_4)^{2^-}$ anions, the spacing is large enough to allow the insertion of the $(WO_4)^{2^-}$ anions. Moreover, electrostatic interaction may exist between negatively charged $(WO_4)^{2^-}$ and positively charged $(Bi_2O_2)^{2^+}$ favoring the insertion of



Fig. 6 Crystal cavity of bismuth terephthalate from CCDC 793572 and the modeled structure of $(WO_4)^{2-}$.

 $(WO_4)^{2-}$. Unfortunately, the crystal of $(WO_4)^{2-}$ -doped bismuth terephthalate suitable for X-ray single crystal diffraction cannot be obtained for the exact location of $(WO_4)^{2-}$.

3.2 Electrochemical and optical performance of the as-prepared samples

Electrochemical analysis has been used to further investigate the effective charge separation and transfer efficiency of the photo-generated carriers over $0.4Na_2WO_4BiBDC$. Fig. 7a shows that the $0.4Na_2WO_4BiBDC$, terephthalate-free sample and BiBDC all exhibited repeatable and relatively stable photocurrents during the successive on/off irradiation cycles, demonstrating their excellent photostability under 3 W LED UV light excitation at a wavelength of 365 nm. The $0.4Na_2WO_4BiBDC$ film coated on ITO glass showed a strong photocurrent response, which is more than twice as strong as that of the terephthalate-free sample and bismuth terephthalate. Therefore, doping of $(WO_4)^{2-}$ has effectively improved the separation of photo-generated carriers and transport of electrons.

The impedance analysis can probe the interfacial charge transfer properties in the absence of light from its data of graphical representation as Nyquist plots. The smaller semicircle diameter of the Nyquist plot indicates a lower charge transfer resistance in the sample. As displayed in Fig. 7b, the relative radii of the plots from different samples can be ranked as follows: $0.4Na_2WO_4BiBDC < BiBDC < 0.3Na_2WO_4BiBDC < 0.1Na_2WO_4BiBDC < 0.5Na_2WO_4BiBDC < control, clearly revealing that doping <math>(WO_4)^{2-}$ can further improve the charge transfer characteristics but offer no information related to the difference in the composition and microstructure between $0.4Na_2WO_4BiBDC$ and $0.3Na_2WO_4BiBDC$. As $0.4Na_2WO_4BiBDC$

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Fig. 7 Transient photocurrents (a) and EIS Nyquist plots (b) of the as-prepared samples.

can facilitate better charge transfer than $0.3Na_2WO_4BiBDC$, it is expected that $0.4Na_2WO_4BiBDC$ should exhibit higher photoreduction activity than $0.3Na_2WO_4BiBDC$.

To probe the semiconductor characteristics of the $(WO_4)^{2^-}$ doped sample, the Mott–Schottky curves shown in Fig. 8a were obtained on $0.4Na_2WO_4BiBDC$ to measure its flat-band potential and determine its semiconductor type. The positive slope of linear potential scan indicates that $0.4Na_2WO_4BiBDC$ is an n-type semiconductor. The flat-band potential was calculated from the *x* intercept of the linear region as -0.01 V relative to Ag/AgCl electrode, equivalent to 0.22 V (*vs.* NHE). For most n-type semiconductors, the potential of conduction band is 0.1 V more negative than the flat band potential; thus, the position of the conduction band is 0.11 V *vs.* NHE.

The optical absorption of the as-prepared samples was analysed by UV-vis DRS to reveal the band gaps of semiconductors and the results are depicted in Fig. 8b and Fig. S5 (in the ESI[†]). All the samples tested are UV light-responsive catalysts. The absorption edge of 0.4Na₂WO₄BiBDC locates at 395 nm. As a rule of thumb, the band gap (E_g) of semiconductor-based photocatalysts can be calculated through the equation: E_{g} = 1240/ λ , where λ is the absorption edge.^{36,37} Thus, the band gap of 0.4Na₂WO₄BiBDC was about 3.14 eV. The band gap energy can also be estimated from the intercept of the tangents of $(ah\nu)^2$ vs. photon energy $(h\nu)$ according to the Kubelka–Munk function. The estimated position of the valence band is 3.25 V vs. NHE ($E_g = E_{VB} - E_{CB}$) and therefore the conduction band is 0.11 V vs. NHE.28 Since the standard redox potential of $Cr(v_I)/(III)$ is +1.33 V vs. NHE, which is more positive than the conduction band of 0.4Na2WO4BiBDC, it allows the photoexcited electrons to reduce Cr(IV) to Cr(III).^{38,39} In theory, the presence of hole scavengers in the Cr(IV) solution can facilitate



Fig. 8 Mott-Schottky curves (a) and diffraction reflectance spectrum (b) of 0.4Na₂WO₄BiBDC (The inset shows its band gap).

the charge separation to accelerate photocatalytic reduction of Cr(IV) by 0.4Na₂WO₄BiBDC.

3.3 Photoreduction of Cr(vi)

Catalytic activities of the as-prepared samples were evaluated by photocatalytic reduction of Cr(vI) (20 mg L⁻¹) to Cr(III) under UV light irradiation to evaluate the effect of $(WO_4)^{2-}$ doping in BiBDC. The results are shown in Fig. 9, where C_0 is the concentration of Cr(vi) after being equilibrated in the dark for 2 h, and C is the concentration of $Cr(v_I)$ in solution at a specific time (min) after UV light irradiation. Fig. 9a shows the reduction efficiencies (C/C_0) of Cr(vi) in the presence of different catalysts after exposure to 180 min of UV light irradiation at room temperature without any hole scavengers added to the solution. The first observation is that the terephthalate-free sample prepared from Na₂WO₄ and Bi(NO₃)₃ shows negligible Cr(vi) reduction efficiency ($\sim 3\%$). The second observation is that bismuth terephthalate achieved higher Cr(vi) reduction efficiency than the terephthalate-free sample but accounted for only 23% of reduced $Cr(v_I)$. The third observation is that $(WO_4)^{2-}$ -doped samples displayed a greater photoreduction activity than undoped BiBDC and the maximum reduction efficiency (70%) was found in 0.4Na₂WO₄BiBDC. Using the first order kinetic model to analyze data in Fig. 9a leads to the rate constants (bar chart) for Cr(vi) reduction by each $(WO_4)^{2-}$ -doped sample (displayed in Fig. 9b) for comparison of reaction rates. Clearly, incorporating $(WO_4)^{2-}$ ions increases the photoreduction rate. An increase in the molar ratio of Na₂WO₄/Bi(NO₃)₃ during synthesis can increase the rate constant but it has a dramatic drop after the ratio of 0.4 as seen in 0.5Na₂WO₄BiBDC. Another interesting aspect from this kinetic study is that the reduction efficiency is not affected by their BET specific surface area.

To elucidate the mechanism related to the photoreduction over 0.4Na₂WO₄BiBDC, various hole scavengers such as citric

acid (CA), triethanolamine (TEOA) and ethylenediaminetetraacetic acid disodium salt (EDTA) all in 1.0 mmol L^{-1} were used as hole scavengers in the photoreduction system.⁴⁰ As shown in Fig. 10a, the rate of photoreduction increases in the following trend: CA > TEOA > EDTA. CA can significantly accelerate the reduction of Cr(vi), in which Cr(vi) was completely reduced within 30 min. But TEOA and EDTA took at least five times longer than CA to reduce Cr(vi) completely. Evidently, the trap of the photoexcited holes can promote the photoexcited electrons to reduce Cr(vi) and CA can promote better than TEOA and EDTA because it has a weaker acid strength (pH = 5). The effect of CA concentration on reduction rate (shown in Fig. 10b) was further investigated with three additional solutions with CA concentrations of 0.5, 1.0 and 3.0 mmol L^{-1} using 0.4Na₂WO₄BiBDC as the catalyst and it was found that there is an inverse linear relationship between the CA concentration and time required for a complete Cr(vi) reduction. Impressively, the reduction of Cr(vi) took only 6 min in the presence of CA (3 mmol L^{-1}). Because of its outstanding performance, 3 mmol L⁻¹ of CA was chosen as the concentration of hole scavenger to further estimate the reduction capability for all other catalyst samples.

Fig. 11 shows the results of photoreduction of Cr(vi) over different samples in the presence of 3 mmol L^{-1} CA. From Fig. 11a, the same amount of Cr(vi) was reduced completely within 18 min in the presence of CA (3 mmol L^{-1}) for all the as-prepared samples. The 0.4Na2WO4BiBDC catalyst exhibits excellent photocatalytic activity to reduce Cr(vi). Because the concentration of CA is much higher than that of Cr(vi), the kinetic model for the reduction of Cr(vi) can be considered as pseudo first order dynamic behavior. The rate constants from the time study on Cr(vi) reduction were calculated (shown in Fig. 11b) with a first order kinetic model. All the $(WO_4)^{2-1}$ doped samples showed accelerated kinetic rates in the presence of CA



Fig. 9 Photoreduction of Cr(vi) under UV light irradiation. C/C₀ versus time plots for reduction of Cr(vi) over different samples within 180 min (a); reduction rate constants of Cr(vi) over different samples (b).



Fig. 10 Reduction of Cr(v) over $0.4Na_2WO_4BiBDC$ under UV light irradiation. In the presence of different hole scavengers with 1 mmol L⁻¹ (a) and the reduction ability (C/C_0) in the presence of CA with different concentrations (b).



Fig. 11 Reduction of Cr(vi) in the presence of 3 mmol L⁻¹ of CA under UV light irradiation (a) and corresponding rate constants of different samples (b).

under UV light irradiation with catalytic efficiencies in the following order: $0.4Na_2WO_4BiBDC > 0.1Na_2WO_4BiBDC > 0.3Na_2WO_4BiBDC > 0.5Na_2WO_4BiBDC$. The maximal rate constant (0.71 min⁻¹) was obtained from $0.4Na_2WO_4BiBDC$. The reaction rate constants for the control and bismuth terephthalate are far less as 0.08 and 0.24 min⁻¹, respectively. Hole scavenger plays a synergic role to enhance the reduction efficiency from 70% (within 180 min in the absence of CA) to 100% (within 6 min in the presence of CA) for $0.4Na_2WO_4$. BiBDC. Moreover, citric acid provides the required acidic condition for the reduction of Cr(v1) to take place.

3.4 Reusability and stability of catalysts

In order to investigate the stability of the $(WO_4)^{2-}$ -doped bismuth terephthalate catalysts during application, $0.3Na_2WO_4$ -BiBDC was chosen as a model catalyst for the photoreduction of Cr(v1) under UV light irradiation. The used catalyst was collected, washed with water and ethanol and dried at 110 °C for reusing. The results of reduction efficiencies, powder XRD patterns and XPS analysis of Cr 2p from four cycles are shown in Fig. S7 (in the ESI[†]). Fig. S7 (ESI[†]) shows that the catalytic activity of $0.3Na_2WO_4BiBDC$ greatly decreased after four recycles. The XRD patterns show that characteristic peaks of 2 θ disappear in the range from 5° to 10° after recycling four times, signifying the disruption of the microstructure in the catalyst, which was attributed to the adsorbed Cr(m) that deactivates the active sites for reduction.⁴¹ The stability of (WO₄)^{2–}-doped bismuth terephthalate catalysts remains a great challenge for further application.

3.5 Plausible reaction mechanism of photocatalytic Cr(vi) reduction

The mechanism of photocatalytic reduction of $Cr(v_l)$ by $(WO_4)^{2-}$ doped bismuth terephthalate catalysts was revealed from a series of experiments performed by controlling three parameters: UV light, the catalyst and the hole scavenger (CA). As summarized in Fig. 12a, there is negligible reduction of $Cr(v_l)$ without a catalyst, UV light irradiation, or CA, reflecting that all these conditions are



Fig. 12 Effects of the scavenger (CA), UV light, and the catalyst on the photoreduction of $Cr(v_1)$ over $0.4Na_2WO_4BiBDC$ (a) and the plausible photoreduction mechanism of $Cr(v_1)$ over $0.4Na_2WO_4BiBDC$ (b).

indispensable to achieve a promising reduction efficiency of $\mathrm{Cr}(v_l)$ within 6 min.

From the electrochemical analysis of $0.4Na_2WO_4BiBDC$, the conduction band (0.11 V) of $0.4Na_2WO_4BiBDC$ is at a potential more negative than the reduction potential of Cr(vi)/(m), making the system favorable for reducing Cr(vi). When UV light was irradiated on $0.4Na_2WO_4BiBDC$, photons with an energy matched with the band gap were absorbed by $0.4Na_2WO_4BiBDC$ and photo-generated carriers were generated. In the presence of citric acid (a hole scavenger), holes are consumed by citric acid to prohibit the electron-hole recombination and promote separation of the photo-generated carriers. Photoexcited electrons transport to the surface of the catalyst and further accelerate the reduction of Cr(vi). This proposed reaction mechanism is summarized in Fig. 12b.⁴²

4. Conclusions

 $(WO_4)^{2-}$ -doped bismuth terephthalate photocatalysts were prepared by a one-pot solvothermal method for the photoreduction of Cr(vi) to Cr(iii) in aqueous solution. The doping amounts of $(WO_4)^{2-}$ were controlled by mixing various molar ratios of precursors $Na_2WO_4/Bi(NO_3)_3$ (n = 0.1, 0.3, 0.4 and 0.5) with a fixed amount of terephthalic acid prior to the solvothermal treatment. The effect derived from the amount of $(WO_4)^{2-}$ doping on the structure, charge transfer characteristics, and photoactivity of BiBDC were systematically studied and it was found that the optimized 0.4Na₂WO₄BiBDC catalyst shows the highest reduction efficiency among all the $(WO_4)^{2-}$ doped samples under UV light irradiation in the presence of 3 mmol L^{-1} citric acid. The reduction efficiency is tripled in comparison to that of undoped bismuth terephthalate. The suitable band gap and good separation of photo-generated electrons and holes are considered to be the main contributing factors for the enhanced performance as they are also key to the proposed mechanism. This report demonstrates the progress towards the synthetic strategy to make conductive layered metal organic frameworks doped by negatively charged $(WO_4)^{2-}$ anions as a viable method to achieve the promising photoreduction catalysts for future sustainable wastewater treatment. Stability of MOFs is expected to develop highly effective multifunctional heterogeneous catalysts for extensively green applications.

Conflicts of interest

There are no conflicts to declare.

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