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1Bismuth Terephthalate Induced Bi⁽⁰⁾ for Enhanced RhB Photodegradation2and 4-Nitrophenol Reduction

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7

8 Abstract

A facile reductive method was used to prepare the semimetal Bi⁽⁰⁾ through reacting 9 $Bi(NO_3)_3$ with NaI. The $Bi^{(0)}$ incorporated bismuth terephthalate hybrids were 10 prepared from two different strategies with enhanced visible light photodegradation of 11 RhB and reduction of 4-nitrophenol. The synergistic interaction between layered 12 bismuth terephthalate and Bi⁽⁰⁾ with SPR effects could induce the effective separation 13 of photogenerated electrons and holes that leading to the enhancement of their 14 oxidation performance. In the reduction of 4-nitrophenol, bismuth terephthalate may 15 act as an excellent supporter and as a precursor which *in situ* produces the semimetal 16 Bi⁽⁰⁾. The Bi⁽⁰⁾ incorporated bismuth terephthalate reported in this work can be 17 potentially applied in visible light photooxidation and reduction of organic 18 compounds. 19

20 Keywords Bi⁽⁰⁾ incorporated bismuth terephthalate; Photodegradation; Reduction of

- 21 4-nitrophenol
- 22
- 23

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2 1. Introduction

Bismuth-based materials have attracted considerable attention due to its nontoxicity, 3 4 low cost and high earth abundance[1]. Bismuth oxyhalides BiOX (X=Cl, Br, I) and their heterostructures [2-10], $BiVO_4$ [11], Bi_2WO_6 [12, 13] nitrogen-doped-5 (BiO)₂CO₃[14] and other bismuth based materials[15-17] were found to exhibit 6 promising photocatalytic activities for the degradation of organic pollutants in waste 7 water. Zero valence bismuth (Bi⁽⁰⁾), as a semimetal with a rhombohedral structure, has 8 been discovered to display appealing applications as it has a very small band gap, a 9 highly anisotropic Fermi surface, and a long carrier mean free path[18]. It can be 10 11 applied in thermoelectricity[19]. It also was involved in many chemical reactions such as the allylation of aldimines [20], transformation of aldehydes to homoallylic 12 alcohols[21], the reduction of aromatic α -halo ketones[22] and nitro compounds[23]. 13 The aerobic oxidation of benzyl alcohol on Pt-Bi/CNT has been reported[24]. In 14 addition, Bi⁽⁰⁾ was reported as a photocatalyst which can enhance the photocatalytic 15 16 oxidation of NO in air[23, 25]. Bismuth also can act as an alternative electron trap in Bi/BiOCl[26-28]. Bi-coupled $Bi_2O_3[29]$, Bi/BiOI[30], Bi/(BiO)_2CO_3[31] and 17 Bi/BiPO₄[32]catalytic systems to degrade organic pollutants and remove Cr(VI) in 18 wastewater[33, 34]. Their higher photocatalytic activities are ascribed to effective 19 separation of photogenerated electron-hole pairs. Bi⁽⁰⁾ has also shown surface 20 plasmon resonance (SPR) effects for enhancing light harvesting[35, 36]. Several 21 methods have been used to prepare semimetal bismuth, including thermal 22 decomposition[37], and electrochemical methods[38]. Simple chemical reduction 23 using a bismuth precursor and different reducing agents such as NaBH₄[39-41], 24 25 hydrazine[42], ethylene glycol [43] and zinc power[44] have also been developed. To date, all these reported synthetic methods are related to high temperature, unavailable 26 precursors including organic bismuth salts, special apparatus or complicated 27 post-processing. Additionally, the capping agents were usually used to enhance its 28

1 stability of elemental bismuth[45]. Therefore, an economically available and facile

2 strategy to prepare stable semimetal bismuth base materials is still urgently needed.

In our early studies [46, 47] a layered bismuth terephthalate was found to act as an 3 4 excellent candidate for preparation of functional materials. But bismuth terephthalate 5 itself has weak photocatalytic activities[7]. In order to further explore the potential of layered bismuth terephthalate as promising catalytic materials and enhance the 6 stability of elemental bismuth, Bi⁽⁰⁾ particles with SPR effects were expected to load 7 into bismuth terephthlate. Herein, we report a simple solvothermal method to prepare 8 semimetal $Bi^{(0)}$ through reacting $Bi(NO_3)_3$ with NaI in *N*,*N*-dimethylformamide (DMF) 9 solution. Bi⁽⁰⁾ incorporated bismuth terephthalate were prepared through two different 10 strategies. The incorporated amounts of Bi⁽⁰⁾ into bismuth terephthalate were tuned by 11 reducing the same amounts of Bi(NO₃)₃ with different amounts of NaI. A one-pot 12 synthesis was performed through in situ reduction of Bi(NO₃)₃ with controlled 13 amounts of NaI (molar ratios of NaI/Bi(NO₃)₃ at 0.5, 0.75 and 1) in the presence of 14 terephthalic acid to give the hybrids BiBDC-I(n) (n = 0.5, 0.75 and 1). A two-step 15 solvothermal method was used by controlling the same molar ratios of NaI/Bi(NO₃)₃ 16 based on the firstly prepared bismuth terephthalate. Their catalytic activities were 17 evaluated on rhodamine B (RhB) photodegradation under visible light and/or UV 18 light irradiation from 350W xenon lamp and reduction of 4-nitrophenol under visible 19 light irradiation from the same xenon lamp or without it at room temperature. Active 20 species involved into RhB photodegradation process under visible light irradiation has 21 been investigated. 22

23 2. Experimental section

24 **2.1 Preparation of catalysts**

25 2.1.1 Preparation of bismuth terephthalate (BiBDC)

The preparation of bismuth terephthalate (BiBDC) was given in our earlier report[46]. In brief, $Bi(NO_3)_3 \cdot 5H_2O$ and terephthalic acid (H₂BDC) were dissolved

into 35 mL of DMF. The resulting mixture was heated at 120°C in a Teflon-lined
stainless steel autoclave for 24 h. The resulting precipitates were collected, washed
with ethanol, water and dried to give 0.38 g of the product which was denoted as
BiBDC.

5 2.1.2 General procedures for the one-pot synthesis of Bi⁽⁰⁾ incorporated BiBDC

This involved dissolving terephthalic acid (0.332 g, 2 mmol) into 15 mL of DMF 6 with stirring. A solution of Bi(NO₃)₃·5H₂O (0.645 g, 1.33 mmol) in 20 mL of DMF 7 8 was prepared by ultrasonic dissolution. Different amounts of NaI with the molar ratios (0.5, 0.75 and 1) of NaI/Bi(NO₃)₃ were added into the above solution of terephthalic 9 acid with stirring. Then the solution of Bi(NO₃)₃ was added slowly into the above 10 mixture with stirring. The final mixture was transferred into a 100 mL Teflon-lined 11 stainless steel autoclave. The subsequent procedure was the same as that used for the 12 preparation of BiBDC. These hybrids were denoted as BiBDC-I(0.5), BiBDC-I(0.75) 13 and BiBDC-I(1), respectively. 14

15 2.1.3 A two-step method for the preparation of Bi⁽⁰⁾ incorporated BiBDC

Bismuth terephthalate (BiBDC, 0.38 g) was prepared firstly, then was dispersed by sonication into 20 mL of DMF with $Bi(NO_3)_3 \cdot 5H_2O$ (0.645 g, 1.33 mmol) and different amounts of NaI with the molar ratios of NaI/Bi(NO₃)₃ at 0.5, 0.75 and 1. The resulting suspension was treated sequentially as done for the BiBDC, and the complexes formed were denoted as BiBDC-I"(0.5), BiBDC-I"(0.75) and BiBDC-I"(1), respectively.

22 2.1.4 Preparation of semimetal bismuth $(Bi^{(0)})$

Semimetal Bi⁽⁰⁾ was prepared according to the one-pot synthesis procedure of Bi⁽⁰⁾
incorporated BiBDC (Experimental section 2.1.2) using Bi(NO₃)₃ (0.645 g, 1.33
mmol) and NaI with the molar ratio of NaI/Bi(NO₃)₃ at 0.75 without terephthalic acid.
Bi⁽⁰⁾ was obtained as black powders.

27 2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance
using Cu Kα radiation. Fourier transform infrared spectra were recorded on a Thermo
Scientific Nicolet NEXUS 4700 spectrometer. X-ray photoelectron spectroscopy

(XPS) measurements were performed on a VG Multilab 2000 photoelectron 1 spectrometer using Al K α radiation as the excitation source under vacuum at 2×10^{-6} 2 Pa. All the binding energy values were calibrated using the C 1s peak at 284.6 eV of 3 the surface adventitious carbon. The morphologies of the samples were investigated 4 by an SU8000 field emission scanning electron microscope (SEM). Transmission 5 electron microscopy (TEM) and high resolution transmission electron microscopy 6 (HRTEM) images were obtained on a Tecnai G20 microscope operated at an 7 8 accelerating voltage of 200 kV. UV-Vis diffuse reflectance spectra (DRS) were measured on a UH4150 spectrophotometer. Photoluminescence measurements were 9 carried out at room temperature on a Hitachi F-7000. Transient photocurrent tests 10 were carried out on CHI760E electrochemical station with a standard three electrode 11 system. The visible light was from a 3W LED lamp. ¹H NMR spectra were recorded 12 on a Varian NMR 400 MHz instrument and the chemical shifts are in ppm and 13 tetramethylsilane as internal standard. 14

15 2.3 Photodegradation of RhB

16 The photocatalytic degradation of RhB (20 mg/L) in aqueous solution (50 mL) was performed under visible light and/or UV light irradiation over as-prepared samples. 17 The reaction temperature was maintained at room temperature by using a 18 double-walled reactor with the circulating water. The visible light was provided by a 19 20 350 W xenon lamp with a 420 nm cutoff filter and UV light was from the same light source using a 365 nm cutoff filter. In each experiment, 50 mg of catalyst was 21 dispersed in RhB solution under sonicated condition for 10 min. The suspension was 22 magnetically stirred in the dark for 2 h for establishment of adsorption equilibrium. 23 24 Then the suspension was irradiated with visible light or UV light. During the given irradiation time, 3 mL aliquots were collected, centrifuged, and filtered through a 25 Millipore filter (pore size 0.45 µm) to remove the residual catalyst. The characteristic 26 absorption of RhB at 553 nm was used to monitor the photodegradation process. 27

28 2.4 Active species trapping experiments over BiBDC-I"(0.75)

Isopropyl alcohol (IPA), benzoquinone (BQ) and ethylenediaminetetraacetic acid disodium salt (EDTA) with final concentrations of 1 mmol/L were added into 50 mL

RhB solution with the concentration of 20 mg/L as active species scavengers[48]. The
 procedure of photodegradation over BiBDC-I"(0.75) was similar to that of RhB
 degradation under visible light irradiation.

4 2.5 Catalytic reduction of 4-nitrophenol

20 mg of the as-prepared catalyst was used to start the 50 mL of reduction system 5 including 1×10^{-4} mol/L of 4-nitrophenol and 1×10^{-2} mol/L of NaBH₄ with visible light 6 irradiation from a 350W xenon lamp or without it at room temperature. The process 7 8 was the same as that used for RhB photodegradation. After NaBH₄ was added into reaction system for 5 min, the catalyst was sequentially added. at specific time 9 interval, 3ml suspensions were taken and filtered through 0.45 µm Millipore filter and 10 the filtrate was analysized intermediately by monitoring the variation of intensity of 11 peak at 400 nm using UV-Vis spectroscopy[45]. The reduction product 12 4-aminophenol was obtained from the filtrate treated with HCl and extracted by ethyl 13 acetate then separated through column chromatography. 14

15 **3. Results and discussion**

16 **3.1 Composition analysis**

All hybrids and Bi⁽⁰⁾ were prepared by a solvothermal method in DMF. BiBDC was 17 used for a comparison. All the XRD diffraction peaks of the prepared Bi⁽⁰⁾ can be 18 readily indexed to a rhombohedral phase of $Bi^{(0)}$ [space group: $R\bar{3}m(166)$, JCPDS No. 19 20 44-1246] and no other diffraction peaks of the impurity are observed (a in Fig. 1B). It is highly crystalline and can be indexed by the representative peaks of (012), (104), 21 (110), (202), (024), (122) planes[49]. The result suggests that semimetal Bi⁽⁰⁾, not 22 bismuth oxide, was obtained in the presence of $Bi(NO_3)_3$ and NaI When the solution 23 of Bi(NO₃)₃ was added slowly into NaI solution at room temperature, an orange-red 24 color occurred. However, neither a color change on potassium iodide-starch test paper 25 nor a black precipitate was observed. This suggested that semimetal Bi⁽⁰⁾ particles 26 were obtained through reduction of the Bi(NO₃)₃ using NaI at a temperature of 120° C, 27 28 not at room temperature. This is ascribed to the stronger reductive ability of Γ . The reduction proceeds to the formation of semimetal Bi⁽⁰⁾ according to the following 29

1 stoichiometry.

2

$2Bi^{3+} + 6I^{-} \longrightarrow 2Bi^{(0)} + 3I_{2} \qquad (1)$

Powder XRD patterns of all the BiBDC-I(n) can be seen in Fig. 1A. They all 3 exhibit characteristic diffraction peaks of Bi⁽⁰⁾. For those hybrids BiBDC-I"(n) (n= 4 0.5, 0.75 and 1) prepared from the two-step method, when NaI with the molar ratio of 5 NaI/ Bi(NO₃)₃ at 0.5 was added, BiBDC-I''(0.5) was formed. But its XRD patterns (b 6 in Fig. 1B) are similar to that of our prepared BiBDC (a in Fig. 1A), i.e. no semimetal 7 Bi⁽⁰⁾ was detected. When the amounts of NaI increased in which the molar ratios of 8 NaI/ Bi(NO₃)₃ varied from 0.75 to 1, semimetal Bi⁽⁰⁾ was formed. So semimetal Bi⁽⁰⁾ 9 were formed from a two-step method by controlling the amounts of NaI with the 10 molar ratios of NaI/ Bi(NO₃)₃ at 0.75 and 1. Overall, Bi⁽⁰⁾ particles were found in five 11 hybrids including BiBDC-I(n) (n=0.5, 0.75, 1), BiBDC-I''(0.75) and BiBDC-I''(1). 12

IR spectra of representative hybrids including semimetal Bi⁽⁰⁾, terephthalic acid and 13 BiBDC can be seen in Fig. 2. It is noted that terephthalic acid has characteristic 14 absorption peaks at 1683.2, 1423.1 and 1286.4 cm⁻¹ (Fig. 2a)[50]. The disappearance 15 of the peak at 1683.2, 1286.4 cm⁻¹ and the concomitant appearance of new peaks 16 located at about 1532.0 and 1382.0 cm⁻¹ for those five hybrids indicate that the 17 -COOH groups of terephthalic acid were completely coordinated with the Bi³⁺ ions in 18 which bismuth terephthalate was formed[7]. Combining with the conclusion from the 19 XRD patterns in which $Bi^{(0)}$ particles exist in the above hybrids, we can safely 20 conclude that Bi⁽⁰⁾ incorporated bismuth terephthalate hybrids were obtained. But for 21 BiBDC-I(0.75) from the one-pot synthesis, absorption peaks at 1562.6 cm⁻¹ (v_{as} 22 C=O) and 1384.7 cm⁻¹ (v_s C=O) were found. For BiBDC-I"(0.75) which was formed 23 from the two-step method, its IR spectrum (Fig. 2b) indicates strong absorption peaks 24 locate at 1533.1 cm⁻¹ and 1384.0 cm⁻¹. The BiBDC-I''(1) has characteristic peaks at 25 1528.9 cm⁻¹ and 1383.7 cm⁻¹. These characteristic absorption peaks of C=O are close 26 to those of BiBDC. However, the frequency of asymmetric stretching vibration of 27 C=O (1562.6 cm⁻¹) for BiBDC-I(0.75) is larger than that for BiBDC-I''(0.75) (1533.1 28 cm⁻¹). The increase in absorption wavenumber for the carbonyl stretching vibration 29

within BiBDC-I(0.75) was attributed that stretching force constant of carbonyl bond 1 increased. It seems that the interactions between Bi⁽⁰⁾ and O atom within BiBDC are 2 weaker for BiBDC-I(0.75) which leads to decreased polarity of C=O bond. It could be 3 ascribed to the less amounts of Bi(NO₃)₃ was used to react with the same amounts of 4 NaI for the preparation of BiBDC-I(0.75). For the one-pot synthesis, Bi(NO₃)₃ plays 5 two different roles in being reduced by NaI and coordinating with terephthlic acid as a 6 nucleating agent. While for the two-step method, the same amounts of Bi(NO₃)₃ was 7 only reduced by the same amounts of NaI (NaI can't reduce the BiBDC at the same 8 conditions). Theoretically, less amounts of Bi⁽⁰⁾ was incorporated into BiBDC-I(0.75). 9 In fact, there is no easy way of quantifying the loading amounts of Bi⁽⁰⁾ owing to the 10 presence of Bi³⁺. 11

The surface chemical compositions and electronic states of BiBDC-I(0.75), 12 BiBDC-I"(0.75) and BiBDC hybrids were further investigated by XPS patterns (Fig. 13 2). The high-resolution Bi 4f spectra show two individual and the same peaks at 159.3 14 eV, 164.5 eV for BiBDC and BiBDC-I(0.75) (Fig. 2c). The corresponding peaks could 15 be attributed to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively [51-53]. The data show oxidation 16 states for Bi is +3. While the Bi 4f spectra of BiBDC-I"(0.75) show two individual 17 peaks at 159.4 eV, 164.7 eV (Fig. 2d). Binding energies of Bi³⁺ within BiBDC-I''(0.75) 18 from the two-step method slightly increase with respect to those of BiBDC-I(0.75). 19 This can be attributed to stronger synergistic interactions between incorporated Bi⁽⁰⁾ 20 and O atom within BiBDC for BiBDC-I"(0.75). This result is consistent with the 21 conclusion from IR data. However, The characteristic peaks of zero valence Bi⁽⁰⁾ at 22 156.8 and 162.1 eV were not observed in the XPS patterns of BiBDC-I"(0.75) as well 23 as those of BiBDC-I(0.75)[54]. The information from the XRD patterns of 24 BiBDC-I(0.75) and BiBDC-I"(0.75) shows that Bi⁽⁰⁾ exists in the hybrids. So it is 25 estimated that most of the Bi⁽⁰⁾ entered into the internal surface of the metal-organic 26 framework BiBDC which can not be detected owing to the limitation of XPS surface 27 technology[55]. This also can be confirmed from SEM and TEM images of those 28 hybrids as shown in Fig. 3. Semimetal Bi⁽⁰⁾ has a granular morphology and BiBDC 29 has a rod like morphology (Fig. S1 in Supporting Information), Bi⁽⁰⁾ incorporated 30

BiBDC hybrids have a similar morphology to that of BiBDC(Fig. 3a-3e). Other 1 information from the TEM images of BiBDC-I"(0.75) demonstrates more details 2 about the interior structure of this hybrid. As can be seen from Fig. 3f-3g, the prepared 3 sample is highly sensitive to electron beam irradiation during the TEM examination 4 due to the relatively low melting point of $Bi^{(0)}$ (273.1 °C), which makes it much more 5 difficult to get clear HRTEM images[44]. The fast Fourier transform (FFT) pattern 6 (Fig. 3h) of high magnification TEM image of Fig. 3g shows lattice fringes with a 7 lattice spacing of about 0.32 nm, which is close to the interplanar spacing of the (012) 8 lattice planes of the rhombohedral bismuth (Bi⁽⁰⁾). Semimetal Bi⁽⁰⁾ really exists in 9 BiBDC-I''(0.75). So BiBDC-I(0.5), BiBDC-I(0.75), BiBDC-I(1), BiBDC-I''(0.75) 10 and BiBDC-I''(1) are regarded as Bi⁽⁰⁾ incorporated BiBDC hybrids. 11



12 13

Fig. 1 XRD patterns of as-prepared samples (A): (a) BiBDC; (b) BiBDC-I(0.5);

14 (c)BiBDC-I(0.75); (d)BiBDC-I(1) and (B): (a) prepared
$$Bi^{(0)}$$
; (b) BiBDC-I''(0.5);

15 (c)BiBDC-I"(0.75); (d)BiBDC-I"(1).



Fig.2 IR spectra of representative samples. BiBDC-I(0.75) and terephthalic acid(a);
BiBDC-I''(0.75), BiBDC-I''(1), prepared Bi⁽⁰⁾ and BiBDC (b); XPS patterns of BiBDC-I(0.75),
BiBDC-I''(0.75) and BiBDC(c), (d).



5

Fig. 3 SEM images of Bi⁽⁰⁾ incorporated BiBDC hybrids. BiBDC-I(0.5) (a); BiBDC-I(0.75)
(b); BiBDC-I(1) (c); BiBDC-I"(0.75) (d); BiBDC-I"(1) (e); TEM image of BiBDC-I"(0.75) (f);

1 TEM image of the region indicated by the box in f (g); The selected area FFT pattern of Fig.3g(h).

2 **3.2 Optical absorption and charge separation**

UV-Vis diffuse reflectance spectra (DRS) were used to investigate the light 3 absorption properties of the as-prepared samples. UV-Vis DRS of BiBDC, Bi⁽⁰⁾, 4 BiBDC-I(n) (n=0.75), and BiBDC-I"(0.75) are shown in Fig. 4. The results from 5 DRS demonstrate that BiBDC has absorption edges at about 350 nm in the UV light 6 region (Fig. 4a). When the semimetal bismuth particles were incorporated into 7 8 bismuth terephthalate, BiBDC-I(n) and BiBDC-I''(n) (n=0.75,1) hybrids exhibit a promising extended absorption edge in the visible light region. Compared with 9 BiBDC-I(0.75), BiBDC-I''(0.75) shows a conspicuously enhanced optical absorption 10 edge which ranges from the UV (350 nm) to the visible light region (650 nm) (Fig. 11 4a). This could be ascribed to a surface plasmon resonance (SPR) effect of Bi⁽⁰⁾ which 12 leading to more visible light harvesting[36]. This enhanced light absorption is crucial 13 for photoexciting more electrons and holes to improve the photodegradation 14 efficiency. 15





Fig. 4 UV-Vis diffuse reflectance spectra of representative hybrids BiBDC-I(0.75),
BiBDC-I''(0.75) and BiBDC, Bi⁽⁰⁾ (a) their photoluminescene emission spectra (b) and transient
photocurrent of representative hybrids (c).

20 Photoluminescence (PL) spectra were further used to investigate the separation 21 efficiency of photoexcited electron-hole pairs for the semiconductor. PL spectra of 22 the representative hybrids BiBDC-I(0.75), BiBDC-I''(0.75), and BiBDC, Bi⁽⁰⁾

excited at 245 nm were recorded (Fig. 4b). Hybrid BiBDC-I''(0.75) shows the lowest 1 PL intensity among all the tested hybrids except the Bi⁽⁰⁾. This implies that the 2 recombination of photoelectrons and holes could be effectively prohibited. In order to 3 further confirm the separation of photocarriers, transient photocurrent test was 4 performed under visible light irradiation from a 3W LED lamp (Fig. 4c). The results 5 show that BiBDC-I''(0.75) has better separation effect than BiBDC. This is attributed 6 to the promotion effect of incorporated Bi⁽⁰⁾ which has a similar Mott-Schottky 7 effect[56]. Bi⁽⁰⁾ was incorporated to build a Schottky barrier at the interface which is 8 beneficial for charge transfer during the separation of photogenerated electrons and 9 holes. 10

11 **3.3 Visible light degradation of RhB**

Photodegradation activities of as-prepared samples were evaluated under visible 12 light irradiation using 20 mg/L of RhB in aqueous solution. The variation of RhB 13 concentration (C/C_0) versus irradiation time t (min) over different samples during the 14 degradation process are shown in Fig. 5, where C and C_0 are the concentration values 15 of RhB at a given time t and 0 min. A blank control assay (without catalysts) was 16 performed for comparison. The direct RhB degradation is negligible under visible 17 light irradiation. When BiBDC was used to degrade 20 mg/L of RhB, the result shows 18 that BiBDC itself has only a weak degradation activity under visible light 19 irradiation[46]. In order to quantitatively evaluate the degradation activities of Bi⁽⁰⁾ 20 incorporated BiBDC and prepared $Bi^{(0)}$, the corresponding reaction rate constants k 21 are determined using a pseudo first-order kinetic model. The results are summarized 22 in Table 1. Compared to BiBDC and Bi⁽⁰⁾, the BiBDC-I(0.75) shows significantly 23 higher RhB photodegradation activities. Thus, the semimetal Bi⁽⁰⁾ was incorporated 24 into BiBDC which can effectively accelerate RhB degradation and enhance the 25 photocatalytic performance of Bi⁽⁰⁾. In order to further improve the catalytic activities 26 of hybrids, a two-step method was used to prepare BiBDC-I''(0.75) and BiBDC-I''(1). 27 Their RhB Degradation results under visible light irradiation are also shown in Fig. 5 28 29 and Table 1. Surprisingly, BiBDC-I''(0.75) and BiBDC-I''(1) both have better degradation activity than that of BiBDC-I(0.75). When the content of incorporated 30

Bi⁽⁰⁾ into BiBDC increased, the photocatalytic process was little hampered. The 1 degradation activity of RhB over BiBDC-I''(1) is lower than that of BiBDC-I''(0.75). 2 This could be ascribed to substantial Bi⁽⁰⁾ covering the interface of BiBDC that 3 prevented the incident photons from impinging on the surface of catalyst, thereby 4 decreasing its photocatalytic performance[57]. This can be confirmed from the results 5 of the lower degradation activity of BiBDC-I(1) compared with that of BiBDC-I(0.75) 6 (Table 1). The reaction rate constants for BiBDC-I''(0.75) and BiBDC-I''(1) are 7 larger relative to those of BiBDC-I(n) (n=0.5, 0.75 and 1) and Bi⁽⁰⁾. Reaction rate 8 constant for BiBDC-I''(0.75) is 6 times than that of Bi⁽⁰⁾ and 4 times than that of 9 BiBDC. A two-step method occurs prior to the one-pot synthesis for the preparation 10 of Bi⁽⁰⁾ incorporated BiBDC. The higher RhB degradation activity of BiBDC-I''(0.75) 11 was attributed to a synergistic interaction between Bi⁽⁰⁾ and the metal-organic 12 framework BiBDC. 13



Fig. 5 Degradation of RhB under visible light irradiation over Bi⁽⁰⁾ incorporated bismuth
 terephthalate.

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- 18
- 19

1 Table 1 Degradation rate constants of RhB over Bi⁽⁰⁾ and Bi⁽⁰⁾ incorporated bismuth

2 terephthalate

Catalysts	Rate constant k
	(min ⁻¹)
Bi ⁽⁰⁾	0.008
BiBDC	0.011
BiBDC-I(0.5)	0.011
BiBDC-I(0.75)	0.019
BiBDC-I(1)	0.014
BiBDC-I''(0.75)	0.048
BiBDC-I''(1)	0.033

3

4 **3.4 Plausible process for RhB degradation**

To further understand the visible light photodegradation process of RhB over the 5 6 BiBDC-I''(0.75), active species trapping experiments were performed. Isopropanol 7 (IPA), benzoquinone (BQ) and ethylenediaminetetraacetic acid disodium salt (EDTA) were used to trap the active hydroxyl radical (\cdot OH), superoxide radical (\cdot O₂) and 8 9 active holes (h^+) involved in the photocatalytic process, respectively[58]. Fig. 6a shows the photodegradation of RhB over BiBDC-I"(0.75) in the absence or presence 10 of scavengers under visible light irradiation. The RhB degradation is markedly 11 suppressed by BQ and EDTA, suggesting that $\cdot O_2^-$ and h⁺ are primarily responsible for 12 RhB degradation. RhB degradation was little inhibited by IPA which suggesting •OH 13 was only involved in the catalytic process to a small degree. The crucial species $\cdot O_2^{-1}$ 14 are produced by reacting O_2 with the separated electrons. It implies that photoexcited 15 electrons and holes play important roles for RhB degradation. Those results from PL 16 17 and transient photocurrent tests further also confirm this hybrid has the excellent 18 separation efficiency of the photogenerated electrons and holes. Thus, the incorporation of the semimetal Bi⁽⁰⁾ into bismuth terephthalate will lead to the 19 formation of a Schottky barrier at the BiBDC-Bi⁽⁰⁾ interface, which is beneficial for 20

1 the charge transferring during the separation of electron-hole pairs.

A possible degradation process of the dye under visible light irradiation can 2 proceed through three possible pathway, i.e. a photolysis process, a dye 3 photosensitization process, or a photocatalytic process[59]. As for RhB, its photolysis 4 process is negligible under visible light irradiation as illustrated in Fig.5[46]. To 5 determine whether a dye photosensitization or photocatalytic process plays a role in 6 7 RhB degradation over BiBDC-I"(0.75), the same degradation procedure was carried 8 out under UV light irradiation. The results are shown in Fig. 6b. Comparing with the 9 results from the visible light irradiation, RhB was degraded completely in 60 minutes under visible light irradiation, while only 75% of RhB was degraded under UV light 10 irradiation with the same irradiation time. Degradation efficiency is higher under 11 visible light irradiation than that under UV light irradiation. This is consistent with the 12 results from DRS of this catalyst which has an extended absorption edge into the 13 visible light region (Fig. 4a). RhB degradation over BiBDC-I''(0.75) under visible 14 light irradiation is a photocatalytic and photosensitization process[60]. Overall, 15 semimetal Bi⁽⁰⁾ with SPR effects was incorporated layered bismuth terephthalate 16 which can effectively enhance the photooxidation efficiency of RhB under visible 17 light irradiation. 18



Fig. 6 Photodegradation of RhB over BiBDC-I"(0.75) in the absence or presence of
 scavengers (BQ, EDTA and IPA) under visible light irradiation (a) and RhB degradation over
 BiBDC-I"(0.75) under visible light and UV light irradiation (b).

4 **3.5 Reduction of 4-nitrophenol**

It was reported that the 4-NP could not be reduced solely by NaBH₄, but in the 5 presence of certain catalyst the reduction reaction can occur [61]. In order to test the 6 catalytic activity of the catalysts in this work on the reduction of 4-NP, a series of 7 reactions were performed. These experiments were carried out in the following 8 conditions: 1) excessive NaBH₄; 2) using Bi⁽⁰⁾ or Bi⁽⁰⁾ incorporated BiBDC and 3) 9 visible light irradiation from 350 W xenon lamp or without it. In these reactions, the 10 4-nitrophenol in aqueous solution (with the weak UV absorption peak at 317 nm) was 11 converted by NaBH₄ to the deep yellow 4-nitrophenolate (with main strong 12 13 absorption peak at 400 nm), which will be eventually reduced to the final the 4-aminophenolate (with absorption peak at 231 nm)[62]. When the as-prepared 14 catalysts were added to the 4-nitrophenolate solution, a fading process of the 15 deep-yellow color of 4-nitrophenolate solution was also observed. Similar 16 characteristic phenomena appeared when the pure phase Bi⁽⁰⁾ was added (Fig. S2 and 17 S3 in Supporting Information). Thus, the reduction process was monitored through 18 the gradually disappearance of this absorbance peak (400 nm). In order to confirm the 19 final product of this reaction, the reduction product 4-aminophenol was obtained by a 20 sequential acidification process and was characterized by ¹H NMR (Fig. S4). Its 21 melting point and ¹H NMR data were consistent with a standard sample. 22

The influence of visible light on the reduction of 4-NP over $Bi^{(0)}$ incorporated bismuth terephthalate hybrids was also investigated (Fig. S5 and S6 in Supporting Information). Depicted in the Fig. 7 are plots of C/C₀ versus time (t) for the reduction of 4-NP in the presence of different catalysts, where C and C₀. mean the concentration of 4-nitrophenolate at t and 5 min after adding of NaBH₄. Since a hundred-fold molar excess of NaBH₄ with respect to the concentration of 4-nitrophenolate was used, the reaction could be considered to follow pseudo-first order kinetics. The reaction rate 1 constant *k* can be derived from the dataset in Fig. 7 by using the following equation.

$$kt = -\ln(C/C_{\theta'}) \tag{2}$$

The obtained rate constants k are collected in Table 2. At a glance of Fig.7, it can 3 be seen that the reductive capability of all Bi⁽⁰⁾ incorporated BiBDC hybrids were 4 more potent than that of Bi⁽⁰⁾. Obviously, the BiBDC composite within these hybrids 5 was responsible for enhanced reduction activities. As can be seen from Table 2, the 6 corresponding rate constants k are ~1.1-2.0 times that of pure $Bi^{(0)}$. The relative low 7 efficiency of pure Bi⁽⁰⁾ may be due to its instability under reduction reaction system. 8 In addition, when white color bismuth terephthalate (BiBDC) was used, some black 9 powder was observed, which was confirmed to be semimetal Bi⁽⁰⁾. Obviously, the 10 black Bi⁽⁰⁾ was in situ generated by the reaction of BiBDC with NaBH₄, and the 11 freshly formed Bi⁽⁰⁾ would sequentially reduce the 4-NP with higher efficiency. We 12 speculated that BiBDC could be a good supporter that was beneficial to the generation 13 of Bi⁽⁰⁾ and the enhancement of reductive capability. Additionally, it can also be seen 14 from Table 2 that under visible light irradiation the catalytic ability of the hybrids 15 from one-pot synthesis such as BiBDC-I(0.5), BiBDC-I(0.75), BiBDC-I(1) successively 16 decreases with the increasing of the incorporated Bi⁽⁰⁾ amount. Similar trends were 17 also observed for those hybrids from two-step method. The present experimental 18 results suggests that visible light irradiation is not beneficial for the enhancing the 19 20 reduction efficiency of 4-nitrophenol over catalyst in this work.



1

Fig. 7 Reduction of 4-NP over Bi⁽⁰⁾ and Bi⁽⁰⁾ incorporated BiBDC with visible light
irradiation or without light irradiation from xenon lamp (C, concentration of 4-nitrophenolate at t
min; C₀, concentration of 4-nitrophenolate after adding of NaBH₄ for 5 min).

Table 2. The rate constants of reduction of 4-NP with visible light irradiation or without light
irradiation from 350 W xenon lamp

samples	Rate constants k (min ⁻¹)	Rate constants k (min ⁻¹) under
	without visible light	visible light irradiation
BiBDC-I(0.5)	0.139	0.150
BiBDC-I(0.75)	0.129	0.115
BiBDC-I(1)	0.166	0.101
BiBDC-I"(0.75)	0.133	0.151
BiBDC-I"(1)	0.145	0.107
Bi ⁽⁰⁾	0.081	0.089
BiBDC	0.144	0.153

7

1 4. Conclusion

In this study, we have introduced a new facile reductive method to prepare 2 semimetal $Bi^{(0)}$ in DMF solution by reacting of $Bi(NO_3)_3$ with NaI at 120°C. 3 Semimetal Bi⁽⁰⁾ incorporated bismuth terephthalate hybrids were prepared from two 4 different methods. A one-pot synthesis was carried out by varying the amounts of NaI 5 with the molar ratios of NaI/Bi(NO₃)₃ at 0.5, 0.75 and 1. A two-step method was used 6 by reacting Bi(NO₃)₃ with controlled amounts of NaI with the molar ratios of 7 NaI/Bi(NO₃)₃ at 0.75 and 1 in the presence of firstly prepared BiBDC. The hybrid 8 BiBDC-I"(0.75) from a two-step method exhibits excellent photodegradation 9 performance towards RhB. Its reaction rate constant is 6 times larger than that of Bi⁽⁰⁾ 10 and 5 times larger than that of BiBDC. The higher visible light degradation activity 11 was attributed to synergistic interaction between Bi⁽⁰⁾ with a surface plasmon 12 resonance and BiBDC which induced more light harvesting and effective separation 13 of electron-hole pairs. The results from active species trapping experiments show 14 that $\cdot O_2^-$ and h⁺ are the most important active species. 15

These Bi⁽⁰⁾ incorporated bismuth terephthalate hybrids also exhibit better reduction capability of 4-nitrophenol than Bi⁽⁰⁾. Visible light and incorporated amount of Bi⁽⁰⁾ significantly affect the catalytic efficiency of 4-NP reduction.

Put all thing together, BiBDC not only acts as an excellent supporter but also as a precursor to *in situ* produce the semimetal Bi⁽⁰⁾ which will sequentially reduce the 4-NP. Thus, Bi⁽⁰⁾ incorporated bismuth terephthalate hybrids were found to be promising visible light catalysts for the removal of organic pollutants and reduction of 4-NP. They can be potentially applied in visible light photooxidation and reduction of organic compounds.

25

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Highlights

- Bi⁽⁰⁾ incorporated bismuth terephthalate were prepared.
- The prepared hybrid exhibits higher visible light photodegradation activity.
- This hybrid also shows better reduction capability of 4-nitrophenol with visible light.
- Visible light inhibited the reduction process of 4-nitrophenol and enhance photooxidation of RhB.

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