Decomposition of Carbon Disulfide Using Dielectric Barrier Discharge Plasma Coupled with Limonite and Siderite Supported Bismuth Vanadate Catalysts

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ABSTRACT

This paper presents the catalytic decomposition of CS₂ using dielectric barrier discharge plasma coupled with novel limonite or siderite supported BiVO₄ composite material (limonite/BiVO₄ or siderite/BiVO₄) prepared via a hydrothermal method. The crystalline structure, surface morphology, gas adsorption properties, and surface chemistry of the catalysts are characterized. The results show that BiVO₄ supported on the limonite or siderite is highly dispersible, which increases its active site. In addition, CS₂ decomposition efficiencies obtained using catalysts fabricated with various Fe/Bi ratios and calcination temperatures are experimentally evaluated. The result show that the maximum CS₂ decomposition efficiencies are obtained using catalysts calcined at 350°C with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7, which respectively yield CS₂ decomposition efficiencies are 11.9% and 13.2% greater than that obtained with dielectric barrier discharge treatment alone. The differences in the CS₂ decomposition efficiencies of the two types of supported catalysts may be due to the chemical and physical differences between limonite and siderite, including the oxidation states of iron and the surface morphology of the iron ores.

Keywords: Dielectric barrier discharge; Supported bismuth vanadate; Carbon disulfide; Catalytic decomposition.

INTRODUCTION

Carbon disulfide (CS₂) is an odorous sulfur compound that has been widely used as important feedstock in the rubber, metallurgy, and viscose fiber industries. However, CS₂ emissions promote photochemical reactions in the stratosphere that represent the primary source of acid rain, which can have harmful effects on the environment and public health (Bates *et al.*, 1992; Tabari *et al.*, 2017). Moreover, CS₂ exposure has been attributed to accelerated atherosclerosis and coronary artery disease (Price *et al.*, 1997; Jia *et al.*, 2017). Common methods of treating CS₂ emissions include adsorption, liquid absorption, condensation, thermo-decomposition, and plasma-based decomposition (Rojo *et al.*, 2010; Pham *et al.*, 2016; Laing *et al.*, 2017). In recent years, plasma-based decomposition technology employing dielectric barrier discharge (DBD) has received considerable attention in the field of hazardous gas treatment due to its significant advantages over conventional CS₂ treatments, such as low cost and milder operation s

conditions, and reduced energy and material consumption (Rojo *et al.*, 2010; Zhu *et al.*, 2013; Albertos *et al.*, 2017; Yang *et al.*, 2017a). However, the decomposition processes in DBD plasma treatment often involve incomplete oxidation reactions, leading to the potential generation of toxic byproducts (Holzer *et al.*, 2002; Li *et al.*, 2017b). This can be addressed by combining plasma decomposition treatment with catalytic processes, which can also significantly improve the energy efficiencies and decomposition performances of the treatments (Krawczyk and Mlotek, 2001; Futamura, 2005; Liu and Liu, 2011; Vandenbroucke *et al.*, 2011; Kirkpatrick *et al.*, 2012). At present, bismuth vanadate (BiVO₄) supported catalysts have been widely used as excellent photocatalysts for waste gas degradation applications. However, the synergistic catalytic treatment of waste gases by combined BiVO₄-supported catalysts and DBD processes has not been widely studied. As such, it warrants additional attention.

BiVO₄ is a new type of photocatalyst that possesses a narrow band gap, good visible light absorption, and stable photo-corrosion resistance (Singh *et al.*, 2016). In addition, BiVO₄ can be converted between three different crystal phases, including tetragonal zircon (z-t), monoclinic scheelite (s-m), and tetragonal scheelite (s-t). The z-t and s-m phases of BiVO₄ possess band gaps of 2.9 eV and 2.4 eV, respectively. As such, the z-t phase of BiVO₄ exhibits optical absorption bands in the ultraviolet (UV) region, while the s-m

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phase exhibits strong optical absorption bands in both the UV and visible regions. This is consistent with the observation that the s-m phase exhibits the highest photocatalytic activity of the three crystalline phases of BiVO_4 (Liu *et al.*, 2016). However, the photocatalytic activity of the s-m phase is limited by the relatively high recombination rate of electron-hole pairs generated in the photolytic process. This has been addressed in many studies by integrating BiVO_4 with supporting materials. For example, Li *et al.* (2015) and Cheng *et al.* (2018) prepared novel hetero-structured $\text{FeVO}_4/\text{BiVO}_4$ composites via a hydrothermal method, and revealed that the photocatalytic activities of the composites are significantly greater than those of either material alone. Chen *et al.* (2017a), Wang *et al.* (2017) and Xiao *et al.* (2018) developed a Cu/BiVO_4 composite photocatalyst that provided an increased photocatalytic activity relative to that of BiVO_4 alone under visible light irradiation. This was speculated to be due to the efficient separation of electron-hole pairs in Cu/BiVO_4 . The previous studies have established that the photocatalytic activity of BiVO_4 is advantageously affected by various properties of the supporting materials, such as nanostructures, high surface area, and high chemical activity (Wang *et al.*, 2017; Wang *et al.*, 2019a, b). These properties are possessed by a number of naturally occurring mineral materials, particularly iron ores, that are widely available and inexpensive (Li *et al.*, 2017a), and are therefore ideal supporting materials for enhancing the photocatalytic activity BiVO_4 for use in large-scale hazardous gas treatment applications.

Siderite (FeCO_3) is a traditional iron mineral resource used in steel smelting. China's siderite resources, with reserves of 2 billion tons, are especially abundant. However, only 10% of the country's siderite reserves have been utilized thus far (Xing *et al.*, 2017; Huang *et al.*, 2017). Limonite is widely present in the epigenetic oxidizing environment and one of the most important components of surface and biochemical activity in soils and sediments (Zou *et al.*, 2013; Zhao *et al.*, 2018).

The present study presents the catalytic decomposition of CS_2 using DBD plasma coupled with novel limonite (main component: $\text{FeO}(\text{OH})$) and siderite (main component: FeCO_3) supported BiVO_4 composite catalysts prepared via a hydrothermal method. The catalysts are subjected to detailed characterization, including their crystalline structure, surface morphology, gas adsorption properties, and surface chemistry. The CS_2 decomposition efficiencies obtained using catalysts fabricated with various Bi/Fe ratios and calcination temperatures are experimentally evaluated. The results demonstrate that the optimum supported BiVO_4 catalysts obtain CS_2 decomposition efficiencies that are substantially greater than that obtained with non-catalyst DBD plasma treatment. The differences in the CS_2 decomposition efficiencies of the two types of supported catalysts are investigated based on the characterization results.

METHODS

Ores and Chemicals

We obtained limonite and siderite rock materials from

Tongling mine, Anhui Province, China. The limonite mainly consists goethite, manganese oxides, and iron (III) oxide hydroxides ($\alpha\text{-FeOOH}$), and bears a porous honeycomb structure generated via the weathering of crystals containing siderite and quartz (Zou *et al.*, 2013). The siderite is formed of sedimentary hematite and metamorphic iron ore deposits, and includes a main fraction of FeCO_3 along with magnesium and manganese elements (Liang *et al.*, 2015). After crushing, the ore was ground into a fine powder and sifted through a 200 mesh sieve. All chemicals were purchased from commercial sources, and were used without further purification. Copper acetate monohydrate, ethylenediamine, triethanolamine, hydrochloric acid, and nitric acid were purchased as analytical grade, and CS_2 and ethanol were purchased with a 99% purity.

Catalyst Preparation

Composite catalysts with limonite/ BiVO_4 and siderite/ BiVO_4 mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1 were synthesized via a previously reported hydrothermal method (Chen *et al.*, 2018), filtered through 200 mesh sieves, and calcined at different temperatures of 250°C, 350°C, 450°C, and 550°C. The hydrothermal synthesis method employed can be briefly outlined as follows. Typically, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.43 g, 5.0 mmol) was added with stirring to an aqueous HNO_3 solution (15 mL, 2.0 mol L^{-1}). The specific iron ore material was then added in an amount based on the specific mass ratio. The mixture was stirred for 0.5 h, yielding Solution A. Solution B was obtained by dissolving NH_4VO_3 (0.58 g, 5.0 mmol) with stirring in the aqueous NaOH solution (15 mL, 2.0 mol L^{-1}). Solution B was slowly added to Solution A under vigorous stirring. The pH of the mixture was adjusted to 5 using an aqueous HCl solution (2 mol L^{-1}). The mixture was stirred for 0.5 h, and transferred to a stainless steel autoclave where it was heated at 180°C for 12 h. The mixture was filtered, and the solid component obtained was washed with distilled water and ethanol. The solid was then dried in a conventional oven at 80°C for 10 h, and calcined at different temperatures for 2 h in a muffle furnace to obtain limonite/ BiVO_4 or siderite/ BiVO_4 composite catalysts.

Characterization Methods

The crystallographic properties of the limonite/ BiVO_4 and siderite/ BiVO_4 composite catalysts were examined by X-ray diffraction (XRD) using a Shimadzu D/Max-rB automatic X-ray diffractometer in a 2θ range of 3° to 70° in 3° min^{-1} . The specific surface areas, N_2 adsorption, and pore sizes of the catalysts were determined using the low temperature N_2 adsorption volumetric method conducted on a Rigaku D/max-2200/PC X-ray diffractometer with approximately 0.3 g of solid sample at a detection temperature of 30.4°C, a cold free space of 48.7 cm^3 , and a degas temperature of 160°C. Scanning electron microscopy (SEM) was conducted using a HITACHI SU-70 analytical ultra-high resolution Schottky thermal field emission scanning electron microscope to analyze the surface microstructure of catalysts after calcination. The surface elements, oxidation states, and bonding environments of the calcined catalysts were analyzed using X-ray photoelectron spectroscopy (XPS)

conducted on a CasaXPS, and XPSPEAK41 was used to conduct peak analysis.

Dielectric Barrier Discharge Plasma

The plasma reactor employed in this study was the standard cylindrical type DBD reactor illustrated in Fig. 1(a). The DBD reactor was customized by the research team. The reactor included two coaxial fused quartz barriers. The outer barrier was a fused quartz tube with an outer diameter of 25 mm and a wall thickness of 1 mm. The inner barrier was a fused quartz tube with an outer diameter of 7 mm and a wall thickness of 1.5 mm. The length of the reactor was 180 mm. The inner electrode was a solid copper rod with a diameter of 3 mm. The outer electrode was composed of a 10 mm band of copper foil wrapped around the external side of the quartz glass tube forming the outer barrier, as shown in Fig. 1(a). The catalyst was first ground and filtered through a 100 mesh sieve, and 1.2 g of the sieved catalyst was mixed with absolute ethanol. The resulting slurry was then applied to the inner surface of an encasing tube and dried at 85°C in a conventional oven. The encasing tube had an outer diameter of 22 mm and a wall thickness of 1 mm, and was positioned coaxially between the inner and outer barriers of the DBD reactor, as illustrated in Fig. 1(b). Simulated flue gas containing a 2000 mg m⁻³ concentration of CS₂ in air as a carrier gas was input at a rate of 0.54 m³ h⁻¹ in the space between the outer and inner barriers in contact with the tubes containing the packed catalyst. The contact area between the catalyst and the flue gas was increased by fabricating the encasing tube with 6 rows of parallel needle-like pyramids placed inside the inner surface of the encasing tube, as shown in Fig. 1(b).

Analysis of CS₂ Treatment

The performance of the proposed CS₂ treatment was evaluated via the decomposition efficiency η , which is the percentage change in the initial concentration of CS₂ (C_0 ; mg m⁻³) in the simulated flue gas and the concentration of CS₂ in the simulated flue gas after treatment (C_1 ; mg m⁻³), and is given as follows:

$$\eta = \frac{C_0 - C_1}{C_0} \times 100\%, \quad (1)$$

$$C = \frac{m \cdot v_1}{v_2 \cdot v_n}, \quad (2)$$

where C is the concentration of CS₂ in the gas to be measured (mg m⁻³), m is the mass of CS₂ dissolved in the sample solution (mg), v_1 is the total volume of sample solution (mL), v_2 is the volume of sample solution used in analysis (mL), and v_n is the volume of the gas sample under standard conditions (m³), which refers to the China GBT 14680-1993 standard: Air quality - Determination of carbon disulfide - Diethylamine spectrophotometric method.

Effect of Catalyst Adsorption of CS₂ on Catalytic Performance

The value of C_1 can be decreased without decomposition by the adsorption of CS₂ on the catalyst. Therefore, we first conducted control experiments to determine the amount of CS₂ adsorbed on the catalyst over time, and thereby evaluate its effect on the overall catalytic performance. To this end, limonite/BiVO₄ (1.2 g, 5:5) and siderite/BiVO₄ (1.2 g, 5:5) composite catalysts calcined at 350°C were individually loaded into the reactor, and the values of C_1 were measured without DBD plasma at different buffer times of 5, 10, 20, 30, 40, and 50 min, and the results compared with C_0 .

Effect of Mass Ratio on the Decomposition Efficiency of CS₂

The values of η obtained for the different limonite/BiVO₄ and siderite/BiVO₄ mass ratios of both limonite/BiVO₄ and siderite/BiVO₄ were evaluated at the different calcination temperatures. Each catalyst was prepared with five limonite/BiVO₄ or siderite/BiVO₄ mass ratios and four calcination temperatures, for a total of 20 samples, and three replicates of each sample were tested. The DBD plasma power output was controlled by adjusting the DBD voltage between the outer and inner electrodes in the range of 5.0 kV to 9.0 kV.

Effect of Calcination Temperature on the Decomposition Efficiency of CS₂

The values of η obtained with both the limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at different temperatures were evaluated for limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7. The DBD voltage was controlled at 6.0 kV.

Fig. 1. Schematic diagrams of the dielectric barrier discharge (DBD) plasma reactor setup: (a) cylindrical DBD reactor; (b) catalyst loading structure.

Analysis of Exhaust Gas

Qualitative analysis of the tail gas obtained from three CS₂ treatment systems: DBD alone, DBD cooperating with limonite/BiVO₄ (mass ratio of 3:7), and DBD cooperating with siderite/BiVO₄ (mass ratio 3:7), was conducted by Fourier transform infrared (FTIR) spectroscopy using a Bruker Vertex 70 spectrometer (Germany). The three CS₂ treatment systems were all implemented under the conditions of a 200 mg m⁻³ CS₂ concentration mixed in air, a 0.54 m³ h⁻¹ intake flow rate, and a DBD voltage adjusted from 5000 V to 9000 V.

Formaldehyde absorption-pararosaniline spectrophotometry (China standard HJ 482-2009) was used to measure the SO₂ concentration in the tail gas, and the standard curve was $y = 0.0234x - 0.0067$ and $R^2 = 0.9991$. The concentration of COS was determined indirectly by spectrophotometry, and the standard curve was $y = 0.0102x - 0.002$ and $R^2 = 0.9954$. The concentrations of CO and CO₂ were determined by infrared spectroscopy.

RESULTS AND DISCUSSION

XRD Analysis

The XRD patterns of limonite/BiVO₄ and siderite/BiVO₄ composite catalysts calcined at 350°C with different limonite/BiVO₄ and siderite/BiVO₄ mass ratios are shown in Figs. 2(a) and 2(b), respectively. The primary reflections for the limonite/BiVO₄ catalysts in Fig. 2(a) are at 2θ values of 19.8°, 29.2°, and 30.5°. The degree of crystallinity (i.e., the grain size) of a sample can generally be gauged according to the intensity and sharpness (i.e., the full width at half maximum; FWHM) of reflections, where the degree of crystallinity increases with increasing intensity and decreasing FWHM. In contrast, the uniformity of the distribution of crystalline grain constituents in a composite sample increases with increasing FWHM. Analysis of the reflections intensities indicates that the highest intensity reflections with the greater FWHM values were obtained at a limonite/BiVO₄ mass ratio of 3:7, which suggests that the

best crystal growth was obtained at this ratio and the BiVO₄ was uniformly distributed at the surface of the limonite support (Zhao *et al.*, 2015). The primary reflections for the siderite/BiVO₄ catalysts in Fig. 2(b) are at 2θ values of 19.4°, 29.8°, and 32.6°. The increase in the reflections intensity and FWHM of the XRD reflections obtained at 2θ values of 19.4°, 29.8°, and 32.6° with increasing BiVO₄ content indicates that the BiVO₄ is uniformly distributed on the siderite support (Chala *et al.*, 2014).

BET Surface Area, N₂ Adsorption, and Pore Size

The N₂ adsorption-desorption isotherm diagrams of the limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C for limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7 are given in Figs. 3(a) and 3(c), respectively, while the corresponding pore size distributions are presented in Figs. 3(b) and 3(d), respectively. These diagrams are also presented in Fig. 3 for the limonite and siderite support materials. The specific surface areas and pore sizes of the supports and catalysts are listed in Table 1. Figs. 3(a) and 3(c) indicate that all supports and catalysts exhibit type III isotherms with H3 hysteresis loops, suggesting mesoporous structures with pore diameters in the range of 2–50 nm (Chen *et al.*, 2017b). At low relative pressures, N₂ is adsorbed and concentrated on the surface, and capillary condensation occurs within the pores as the relative pressure increases, which yields curves with sharply increasing slopes and hysteresis loops in the diagrams. This indicates that the combination of BiVO₄ and limonite or siderite to form composites increased the pore diameter relative to the supports alone. Figs. 3(b) and 3(d) indicate that the pore diameters of the supports and catalysts are between 2.0 nm and 10 nm, which confirms that these materials have mesoporous structures. As shown in Table 1, both limonite/BiVO₄ and siderite/BiVO₄ exhibited greater specific surface areas and pore volumes than the corresponding support materials. This indicates that BiVO₄ loading altered the pore structure of limonite and siderite, and increased the surface area, and thus increased the concentration of active sites.

Fig. 2. X-ray diffraction spectra of the composite catalysts calcined at 350°C with different limonite/BiVO₄ and siderite/BiVO₄ mass ratios: (a) limonite/BiVO₄; (b) siderite/BiVO₄.

Fig. 3. N₂ adsorption-desorption isotherm diagrams (a) and (c), and pore size distributions (b) and (d) of limonite and siderite supports and limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7.

Table 1. Specific surface areas and pore sizes of different iron ore supports and composite catalysts with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7.

Sample	Specific surface area (m ² g ⁻¹)	Pore volume (×10 ⁻² cm ³ g ⁻¹)	Pore diameter (nm)
Limonite	35.25	9.98	3.818
Limonite/BiVO ₄	48.46	13.28	3.830
Siderite	3.55	0.82	3.826
Siderite/BiVO ₄	10.67	2.94	3.818

TG-DTG

The differential thermogravimetric (DTG) and thermogravimetric (TG) curves of siderite in a N₂ atmosphere are shown in Fig. 4. Four major mass change steps between 30 and 800°C are apparent in the TG curve. Combination of the DTG and TG curve data reveals that the mass step changes can be attributed to different reasons. The mass loss occurring between 30 and 277.40°C (1.345%); as observed in the DTG curve is due to the conversion of goethite into hematite caused by dehydroxylation (Xing et

al., 2017). The mass gain occurring between 277.40 and 469.12°C (2.078%) is due to the oxidation of FeO to CO₂ in N₂ prior to the decomposition of the siderite. The mass loss occurring between 469.12 and 673.96°C (14.94%) is attributed to the conversion of siderite into Fe₃O₄, which releases a large amount of CO. Finally, the mass loss between 673.96 and 800°C (1.249%) is due to the thermal decomposition of residual structural hydroxyl groups. TG analysis indicates that goethite is present in fresh siderite samples.

Fig. 4. Thermal gravimetric analysis of siderite.

SEM

Figs. 5 and 6 respectively present SEM images of limonite/ BiVO_4 and siderite/ BiVO_4 catalysts calcined at 350°C with limonite/ BiVO_4 and siderite/ BiVO_4 mass ratios of 3:7 (a–c) and 5:5 (d–f). It can be observed from Fig. 5(c) that the limonite surface in the limonite/ BiVO_4 catalyst (mass ratio of 3:7) was covered by a smooth layer, and a partially petal shaped morphology is observed, which further suggests that BiVO_4 was uniformly distributed on the limonite surface. The SEM images of the limonite/ BiVO_4 catalyst (mass ratio of 5:5) exhibit similar morphologies as

those observed for the limonite/ BiVO_4 (3:7) catalyst. However, a comparison of Figs. 5(a) and 5(d) suggests that the 3:7 catalyst provides a greater surface area with smoother surfaces and more irregular shapes than the 5:5 catalyst. This may promote interaction between gas precursors and BiVO_4 catalysts on iron ore supports. This can be expected to facilitate the interactions of more BiVO_4 catalyst loaded to iron ore support (Guan *et al.*, 2010). In addition, comparison of Figs. 5(a) and 5(d) indicates that the 5:5 catalyst presents a different local stacking morphology than the 3:7 catalyst, which suggests the presence of some impurities in the limonite support material. Similar results are observed for the siderite/ BiVO_4 catalysts in Fig. 6. Smooth spherical particles are again observed on the siderite surface in Fig. 6(c), suggesting that BiVO_4 was uniformly distributed on the siderite surface (Yu *et al.*, 2014). However, aggregations of spherical particles with high intensity detected electron signals are observed in Figs. 6(d) and 6(e), which are indicative of BiVO_4 catalyst aggregations at a mass ratio of 5:5. Overall, the SEM images indicate that both limonite/ BiVO_4 and siderite/ BiVO_4 composite catalysts exhibit better BiVO_4 distributions for a mass ratio of 3:7.

XPS

The XPS survey scan spectra of the limonite and siderite supports calcined at 350°C indicate the existence of O, Fe, and C elements, while O, Fe, C, V, and Bi elements were detected in the limonite/ BiVO_4 and siderite/ BiVO_4 composite catalysts with mass ratios of 3:7 calcined at 350°C high

Fig. 5. Scanning electron microscopy images of limonite/ BiVO_4 catalysts calcined at 350°C for different limonite/ BiVO_4 mass ratios: (a), (b), and (c) 3:7 with magnifications of 100000, 250000, and 500000 times, respectively; (d), (e), and (f) 5:5 with magnifications of 100000, 250000, and 500000 times, respectively.

Fig. 6. Scanning electron microscopy images of siderite/ BiVO_4 catalysts calcined at 350°C for different siderite/ BiVO_4 mass ratios: (a), (b), and (c) 3:7 with magnifications of 100000, 250000, and 500000 times, respectively; (d) and (e) 5:5 with magnifications of 500000 and 250000 times, respectively.

resolution Fe 2p spectra are presented in Fig. 7(a) for limonite/ BiVO_4 (top) and limonite (bottom), and the Bi 4f spectrum for limonite/ BiVO_4 is presented in Fig. 7(b). The spectra in Fig. 7(a) are fitted, and the binding energies of the Fe 2p_{3/2} and Fe 2p_{1/2} electron states are labeled. Comparison of the fitted Fe 2p spectra of limonite/ BiVO_4 and limonite indicates that combining the support with BiVO_4 increases the binding energy of Fe, suggesting that the introduction of BiVO_4 altered the electron density of the Fe sites (Liu *et al.*, 2017). Similarly, high resolution Fe 2p spectra are presented and fitted in Fig. 6(c) for siderite/ BiVO_4 (top) and siderite (bottom), and the Bi 4f spectrum for siderite/ BiVO_4 is presented and fitted in Fig. 6(d). The two major peaks obtained for the siderite/ BiVO_4 catalyst at 708.7 eV and 722.5 eV corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} electron states are consistent with the Fe^{3+} oxidation state (Ji *et al.*, 2015). However, in this case, combining the siderite support with BiVO_4 very slightly decreased the binding energies of the Fe 2p_{3/2} and Fe 2p_{1/2} electron states. This may lead to a greater electron deficiency and a stronger reduction ability (Yang *et al.*, 2017b). The binding energy of 156.6 eV assigned to the Bi 4f_{5/2} electron state of limonite/ BiVO_4 in Fig. 7(b) is consistent with the Bi^{3+} oxidation state (Kong *et al.*, 2013), while the binding energy of 162 eV assigned to the Bi 4f electron state suggests a higher oxidation state of Bi^{5+} (Huang *et al.*, 2010). It can be observed that in the high resolution XPS spectrum of limonite/ BiVO_4 overlap with some shoulder peaks indicative of varying chemical environments for the Bi sites (Lamdab *et al.*, 2016). In

contrast, the binding energies of the Bi 4f electron states of siderite/ BiVO_4 exhibited no overlapping shoulder peaks. The appearance of overlapping shoulder peaks in Fig. 7(b) may be the result of impurities in the naturally occurring limonite. Here, we note that the collected limonite exhibited a lower purity than the siderite, and thus impurity elements may affect the binding energies of the Bi 4f electron states after forming the limonite/ BiVO_4 composite catalysts.

Adsorption Equilibrium of CS_2 Absorbed by Limonite/ BiVO_4 and Siderite/ BiVO_4 Catalysts without DBD

The CS_2 concentration change over time obtained in the CS_2 adsorption control experiments are plotted in Fig. S1. These results indicate that the CS_2 concentration in reactions involving both the limonite/ BiVO_4 and siderite/ BiVO_4 catalysts reached equilibrium inside the reactor after a buffer time of 30 min. Therefore, all further research conducted in conjunction with plasma discharge was conducted after a 30 min pre-equilibrium period.

Effect of Mass Ratio on CS_2 Decomposition Efficiency

The values of η obtained as a function of DBD voltage for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/ BiVO_4 and siderite/ BiVO_4 catalysts calcined at 350°C with different limonite/ BiVO_4 and siderite/ BiVO_4 mass ratios are shown in Figs. 8(a) and 8(b), respectively. The differences between the values of η obtained in the coupled and non-coupled treatments were

Fig. 7. High resolution Fe 2p spectra of the supports and Fe 2p and Bi 4f spectra of the composite catalysts: (a) Fe 2p spectra for limonite/BiVO₄ (top) and limonite (bottom); (b) Bi 4f spectrum for limonite/BiVO₄; (c) Fe 2p spectra for siderite/BiVO₄ (top) and siderite (bottom); (d) Bi 4f spectrum for siderite/BiVO₄.

greatest for a DBD voltage of 6.0 kV. Compared with DBD plasma treatment alone, the maximum increases in η obtained with DBD plasma coupled with the limonite/BiVO₄ catalysts were 8.1%, 11.9%, 5.6%, 5.7%, and 3.7% for mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1, respectively. Similarly, the maximum increases in η obtained with DBD plasma coupled with the limonite/BiVO₄ catalysts were 8.6%, 13.2%, 6.1%, 4.4%, and 4.1% for mass ratios of 1:9, 3:7, 5:5, 3:7, and 9:1, respectively.

We also note from Fig. 8 that value of η increased with increasing BiVO₄ content up to a maximum at the mass ratio of 3:7, which provided the best value of η at any DBD voltage for both limonite/BiVO₄ and siderite/BiVO₄ catalysts, and then decreased for a mass ratio of 9:1. This can be explained according to the distribution of the BiVO₄ catalyst. An appropriate mass ratio can ensure that BiVO₄ is uniformly distributed over the supporting materials (Huang *et al.*, 2015). A low BiVO₄ content facilitates the equal distribution of BiVO₄ over the available active sites, and more surface becomes covered with an equal distribution of

BiVO₄ as the BiVO₄ content increases. However, with further increasing BiVO₄ content greater than a mass ratio of 3:7, excess BiVO₄ is stacked on the surfaces of the support materials, which covers the catalytic active site and decreases the decomposition efficiency (Sriwichai *et al.*, 2014). In addition, the band gaps of the limonite and siderite supports can affect the decomposition efficiency. Here, limonite and siderite possess narrow band gaps, which can facilitate the transfer of electrons and holes from the conduction and valance bands of BiVO₄, and thereby inhibit the annihilation of electron-hole pairs within BiVO₄ (Wang *et al.*, 2016; Wang *et al.*, 2017; Xia *et al.*, 2017).

The results in Fig. 8 can be included with the results shown in Figs. S2 and S3 to compare the values of η obtained as a function of DBD voltage for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/BiVO₄ and siderite/BiVO₄ catalysts with different mass ratios under calcination temperatures of 250°C, 350°C (Fig. 7), 450°C, and 550°C. We note that the variations in η with respect to the DBD voltage for the

Fig. 8. CS₂ decomposition efficiency (η) for catalysts calcined at 350°C with different limonite/BiVO₄ and siderite/BiVO₄ mass ratios: (a) limonite/BiVO₄; (b) siderite/BiVO₄.

different calcination temperatures represent similar trends as those obtained at 350°C in Fig. 7.

Effect of Calcination Temperature on CS₂ Decomposition Efficiency

Fig. 9 present the increases in the values of η compared with DBD treatment alone obtained for coupled DBD plasma treatment at a DBD voltage of 6.0 kV using the limonite/BiVO₄ and siderite/BiVO₄ catalysts with a mass ratio of 3:7 under different calcination temperatures. Here, we note that the increases in the values of η first increased with increasing calcination temperature, and then decreased after reaching peak performance at 350°C for both catalysts. This trend can be related to changes in the crystal structure of the catalysts at different calcination temperatures. The optimal calcination temperature of BiVO₄ lies between 300°C and 400°C, although the higher temperature in this range can lead to changes in the crystal morphology (Zhao *et al.*, 2012; Yuan *et al.*, 2015; Xia *et al.*, 2017). The limonite and siderite support materials, as well as the composites, also suffer from disadvantageous changes in the surface area and pore size under higher calcination temperatures owing to pore space collapse and BiVO₄ catalyst aggregation, resulting in decreased catalytic performance (Liu and Zhou, 2015).

Comparison of CS₂ Treatment Involving Limonite and Siderite Supports

The values of η obtained as a function of DBD voltage in Fig. 8 for DBD plasma treatment alone and for coupled DBD plasma treatment with the limonite/BiVO₄ and siderite/BiVO₄ catalysts calcined at 350°C with a mass ratio of 3:7 are presented in Fig. S4 to facilitate detailed

comparison. Compared with DBD plasma treatment alone at a DBD voltage of 6.0 kV, coupled DBD plasma treatment with the siderite/BiVO₄ catalyst increased the value of η by 13.2%, while coupled DBD plasma treatment with the limonite/BiVO₄ catalyst increased the value of η by 11.9%. This small difference could be due to the structural and compositional differences between limonite and siderite. The results of additional experiments being conducted presently to study the effect of catalyst structure and composition on CS₂ decomposition performance will be reported in the future.

Analysis of Exhaust Gas

The exhaust gas FTIR spectrum is shown in Fig. 10. Here, the peak at 1373 cm⁻¹ represents S=O bond stretching vibrations (Rudakova *et al.*, 2003), indicating that the substance is SO₂, the peak at 2345 cm⁻¹ represents C=O bond stretching vibrations, indicating that the substance is CO₂, the peak at 2100 cm⁻¹ represents C and O triple bond stretching vibrations (Chen *et al.*, 2007), indicating that the substance is CO, the peak near 2084 cm⁻¹ represents stretching vibrations for the C=O bond of COS (Yan *et al.*, 2013), and the peak at 1015 cm⁻¹ is an O₃ absorption peak, indicating that the intermediate products of CS₂ degradation are SO₂, CO, CO₂, and COS.

Fig. 11 shows that the concentrations of SO₂, CO, CO₂, and COS in the exhaust gas for all treatments increase with increasing DBD voltage. Here, CS₂ receives energy in the process of reactor discharge, and is stimulated to produce intermediate products, such as CS*, active group O₃⁻, OH⁻, and O₃. These intermediate products can then form additional products, where CS* and O₂ can produce SO₂, S and O₂ can produce SO and then react with O₂ to produce SO₂, CS and O₂ can produce COS and O, and O reacts with SO₂ to

Fig. 9. Values of η for catalysts with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7 obtained under different calcination temperatures.

Fig. 10. Fourier transform infrared spectrum of exhaust gas.

produce CO and CO₂. An increasing concentration of CS and active groups O, O₂, and O₃ are generated with increasing DBD voltage, resulting in the production of increased concentrations of SO₂, COS, and carbon oxides. The concentrations of SO₂, CO, and COS in the tail gas of the DBD combined with catalyst treatments are less than those obtained by DBD treatment alone, but the concentration of CO₂ is greater than that obtained by DBD treatment alone. Under a DBD voltage of 9000 V, the concentrations of SO₂, CO, COS, and CO₂ in the tail gas obtained for DBD treatment alone were 121.4 mg m⁻³, 106.3 mg m⁻³, 62.7 mg m⁻³, and 80.5 mg m⁻³, respectively, while these were 104.7 mg m⁻³, 89.0 mg m⁻³, 56.1 mg m⁻³, 100.9 mg m⁻³, respectively, under

the DBD cooperating with limonite/BiVO₄ (mass ratio 3:7) treatment, and 87.1 mg m⁻³, 81.9 mg m⁻³, 49.6 mg m⁻³, and 103.6 mg m⁻³, respectively, under the DBD cooperating with siderite/BiVO₄ (mass ratio of 3:7) treatment. Therefore, compared with DBD cooperating with limonite/BiVO₄, DBD cooperating with siderite/BiVO₄ produced a greater concentration of CO₂, and smaller concentrations of SO₂, CO, and COS.

Comparison with Other CS₂ Treatments

Compared with a previously reported coupled DBD plasma MnO₂ catalytic CS₂ treatment system, the proposed coupled DBD CS₂ treatment system employing limonite/BiVO₄ and

Fig. 11. Changes in SO₂, COS, CO₂, and CO concentrations in the tail gas under different DBD voltage treatments: (a) SO₂; (b) COS; (c) CO₂; (d) CO.

siderite/BiVO₄ catalysts calcined at 350°C with a mass ratio of 3:7 exhibited η values that were around 5% greater under equivalent reaction conditions. This could be due to the close energy band interactions of the BiVO₄ photocatalyst with the supporting iron ore materials that prolonged the lifetime of the activated oxygen species by inhibiting the annihilation of electron-hole pairs within BiVO₄. The CS₂ decomposition efficiency is also enhanced relative to that of the MnO₂ catalytic system by the high surface area and better porous structure of the supporting materials, which facilitates the equal distribution of catalytic active sites.

CONCLUSIONS

This study developed an efficient CS₂ decomposition method based on DBD plasma coupled with a novel BiVO₄ photocatalyst supported by a limonite (FeO(OH)) or siderite (FeCO₃) iron ore material. The catalyst was synthesized via a hydrothermal method. The effects of the limonite/BiVO₄ and siderite/BiVO₄ mass ratios and calcination temperature

on the CS₂ decomposition efficiency of DBD plasma coupled with the limonite/BiVO₄ and siderite/BiVO₄ composite catalysts were experimentally investigated using a standard DBD plasma reactor. The optimum composition for both composite catalysts was obtained at a calcination temperature of 350°C with limonite/BiVO₄ and siderite/BiVO₄ mass ratios of 3:7. The results of DBD plasma coupled with the optimum limonite/BiVO₄ and siderite/BiVO₄ composite catalysts demonstrated increased CS₂ decomposition efficiencies of 11.9% and 13.2%, respectively, relative to that of DBD plasma alone. The slightly better performance of the siderite/BiVO₄ composite catalyst than limonite/BiVO₄ could be due to the composition of the limonite and siderite iron ores. The main components of the tail gas after DBD synergistic catalytic treatment of CS₂ were SO₂, COS, CO, and CO₂. The catalyst can increase the oxidizing species of the discharge system, and ensure the more thorough oxidation of SO₂ and COS, resulting in smaller concentrations of SO₂, COS, and CO, and greater concentrations of CO₂ in the tail gas. Future study will focus on how minor elements and the

morphology of the supporting materials affect the CS₂ decomposition efficiency of the composite catalysts.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

DISCLAIMER

The authors declare no competing financial interest.

REFERENCES

- Albertos, I., Martín-Diana, A.B., Cullen, P.J., Tiwari, B.K., Ojha, S.K., Bourke, P., Álvarez, C., Rico, D. and Technologies, E. (2017). Effects of dielectric barrier discharge (DBD) generated plasma on microbial reduction and quality parameters of fresh mackerel (*Scomber scombrus*) fillets. *Innovative Food Sci. Emerg. Technol.* 44: 117–122.
- Bates, T.S., Lamb, B.K., Guenther, A., Dignon, J. and Stoiber, R.E. (1992). Sulfur emissions to the atmosphere from natural sources. *J. Atmos. Chem.* 14: 315–337.
- Chala, S., Wetchakun, K., Phanichphant, S., Inceesungvorn, B. and Wetchakun, N. (2014). Enhanced visible-light-response photocatalytic degradation of methylene blue on Fe-loaded BiVO₄ photocatalyst. *J. Alloys Compd.* 597: 129–135.
- Chen, F., Yang, Q., Li, X., Zeng, G., Wang, D., Niu, C., Zhao, J., An, H., Xie, T. and Deng, Y. (2017b). Hierarchical assembly of graphene-bridged Ag₃PO₄/Ag/BiVO₄ (040) Z-scheme photocatalyst: An efficient, sustainable and heterogeneous catalyst with enhanced visible-light photoactivity towards tetracycline degradation under visible light irradiation. *Appl. Catal.* 200: 330–342.
- Chen, H., Kong, L., Chen, J., Zhang, R. and Wang, L. (2007). Heterogeneous uptake of carbonyl sulfide on hematite and hematite-NaCl mixtures. *Environ. Sci. Technol.* 41: 6484–6490.
- Chen, R., Zhu, C., Lu, J., Xiao, J., Lei, Y. and Yu, Z. (2018). BiVO₄/α-Fe₂O₃ catalytic degradation of gaseous benzene: Preparation, characterization and photocatalytic properties. *Appl. Surf. Sci.* 427: 141–147.
- Chen, Y., Wang, M., Du, X., Ran, J., Zhang, L. and Tang, D. (2017a). High Resistance to Na Poisoning of the V₂O₅-Ce(SO₄)₂/TiO₂ Catalyst for the NO SCR Reaction. *Aerosol Air Qual. Res.* 12: 2948–2955.
- Cheng, S.W., Li, Y.H., Yuan, C.S., Tsai, P.Y., Shen, H.Z. and Hung, C.H. (2018). An innovative advanced oxidation technology for effective decomposition of formaldehyde by combining iron modified nano-TiO₂ (Fe/TiO₂) photocatalytic degradation with ozone oxidation. *Aerosol Air Qual. Res.* 12: 3220–3233.
- Futamura, S. (2005). VOCs removal with nonthermal plasma and catalysts. *J. Jpn. Inst. Energy* 84: 474–479.
- Guan, M.L., Ma, D.K., Hu, S.W., Chen, Y.J. and Huang, S.M. (2010). From hollow olive-shaped BiVO₄ to n-p core-shell BiVO₄@Bi₂O₃ microspheres: Controlled synthesis and enhanced visible-light-responsive photocatalytic properties. *Inorg. Chem.* 50: 800–805.
- Holzer, F., Roland, U. and Kopinke, F.D. (2002). Combination of non-thermal plasma and heterogeneous catalysis for oxidation of volatile organic compounds: Part 1. Accessibility of the intra-particle volume. *Appl. Catal. B* 38: 163–181.
- Huang, C.M., Pan, G.T., Peng, P.Y. and Yang, T.C. (2010). In situ DRIFT study of photocatalytic degradation of gaseous isopropanol over BiVO₄ under indoor illumination. *J. Mol. Catal. A* 327: 38–44.
- Huang, H., Liu, L., Zhang, Y. and Tian, N. (2015). Novel BiO₄/BiVO₄ composite photocatalyst with highly improved visible-light-induced photocatalytic performance for rhodamine B degradation and photocurrent generation. *RSC Adv.* 5: 1161–1167.
- Huang, Y., Cao, J.J., Kang, F., You, S.J., Chang, C.W. and Wang, Y.F. (2017). High selectivity of visible-light-driven La-doped TiO₂ photocatalysts for NO Reoval. *Aerosol Air Qual. Res.* 10: 2555–2565.
- Ji, K., Dai, H., Deng, J., Zang, H., Arandiyani, H., Xie, S. and Yang, H. (2015). 3DOM BiVO₄ supported silver bromide and noble metals: High-performance photocatalysts for the visible-light-driven degradation of 4-chlorophenol. *Appl. Catal. B* 168: 274–282.
- Jia, J., Cheng, S., Liu, L., Lang, J., Wang, G., Chen, G. and Liu, X. (2017). An integrated WRF-CAMx Modeling approach for impact analysis of implementing the emergency PM_{2.5} control measures during red alerts in Beijing in December 2015. *Aerosol Air Qual. Res.* 10: 2491–2508.
- Kirkpatrick, M. J., Odic, E., Zinola, S. and Lavy, J. (2012). Plasma assisted heterogeneous catalytic oxidation: HCCI diesel engine investigations. *Appl. Catal. B* 117: 1–9.
- Kong, L., Jiang, Z., Lai, H.C., Xiao, T. and Edwards, P.P. (2013). Does noble metal modification improve the photocatalytic activity of BiOCl? *Prog. Nat. Sci.* 23: 286–293.
- Krawczyk, K. and Mlotek, M. (2001). Combined plasma-catalytic processing of nitrous oxide. *Appl. Catal. B* 30: 233–245.
- Laing, J., Jaffe, D.A., Slavens, A.P., Li, W. and Wang, W. (2017). Can ΔPM_{2.5}/ΔCO and ΔNO_y/ΔCO enhancement ratios be used to characterize the influence of wildfire smoke in urban areas. *Aerosol Air Qual. Res.* 10: 2413–2423.
- Lamdab, U., Wetchakun, K., Phanichphant, S.,

- Kangwansupamonkon, W. and Wetchakun, N. (2016). InVO₄-BiVO₄ composite films with enhanced visible light performance for photodegradation of methylene blue. *Catal. Today* 278: 291–302.
- Li, J., Zhao, W., Guo, Y., Wei, Z., Han, M., He, H., Yang, S. and Sun, C. (2015). Facile synthesis and high activity of novel BiVO₄/FeVO₄ heterojunction photocatalyst for degradation of metronidazole. *Appl. Surf. Sci.* 351: 270–279.
- Li, Q., Liu, H., Chen, T., Chen, D., Zhang, C., Xu, B., Zhu C. and Jiang, Y. (2017a). Characterization and SCR performance of nano-structured iron-manganese oxides: Effect of annealing temperature. *Aerosol Air Qual. Res.* 17: 2328–2337.
- Li, Y., Yang, L., Chen, X., Gao, Y., Jiang, Pan., Zhang, J., Yu, H. and Wang, W. (2017b). PM_{2.5}-bound PAHs in indoor and outdoor of hotels in urban and suburban of Jinan, China: Concentrations, sources, and health risk impacts. *Aerosol Air Qual. Res.* 10: 2463–2473.
- Liang, H., Chen, W., Wang, R., Qi, Z., Mi, J. and Wang, Z. (2015). X-shaped hollow α -FeOOH penetration twins and their conversion to α -Fe₂O₃ nanocrystals bound by high-index facets with enhanced photocatalytic activity. *Chem. Eng. J.* 274: 224–230.
- Liu, H.X. and Liu, Y. (2011). Removal of *P-Xylene* by a DBD-type plasma combined with catalyst. *Environ. Eng. Manage.* 10: 749–753.
- Liu, S., Tang, H., Zhou, H., Dai, G. and Wang, W. (2017). Photocatalytic performance of sandwich-like BiVO₄ sheets by microwave assisted synthesis. *Appl. Surf. Sci.* 391: 542–547.
- Liu, Y., Yin, Y., Jia, X., Cui, X., Tian, C., Sang, Y. and Liu, H. (2016). Synthesis process and photocatalytic properties of BiOBr nanosheets for gaseous benzene. *Environ. Sci. Pollut. Res.* 23: 17525–17531.
- Liu, Z. and Zhou, C. (2015). Improved photocatalytic activity of nano CuO-incorporated TiO₂ granules prepared by spray drying. *Prog. Nat. Sci.* 25: 334–341.
- Pham, T.D., Lee, B.K. and Lee, C.H. (2016). The advanced removal of benzene from aerosols by photocatalytic oxidation and adsorption of Cu-TiO₂/PU under visible light irradiation. *Appl. Catal. B.* 182: 172–183.
- Price, B., Bergman, T.S., Rodríguez, M., Henrich, R.T. and Moran, E.J. (1997). A review of carbon disulfide exposure data and the association between carbon disulfide exposure and ischemic heart disease mortality. *Regul. Toxicol. Pharm.* 26: 119–128.
- Rojo, N., Gallastegui, G., Barona, A., Gurtubay, L., Ibarra-Berastegi, G. and Elías, A. (2010). Biotechnology as an alternative for carbon disulfide treatment in air pollution control. *Environ. Rev.* 18: 321–332.
- Rudakova, A.V., Lobo, R.F. and Bulanin, K.M. (2003). FT-IR study of carbon monoxide adsorption on Li-exchanged zeolite X. *J. Phys. Chem.* 107: 5212–5220.
- Singh, P., Ojha, A., Borthakur, A., Singh, R., Lahiry, D., Tiwary, D. and Mishra, P.K. (2016). Emerging trends in photodegradation of petrochemical wastes: A review. *Environ. Sci. Pollut. Res.* 23: 22340–22364.
- Sriwichai, S., Ranwongsa, H., Wetchakun, K., Phanichphant, S. and Wetchakun, N. (2014). Microstructures. Effect of iron loading on the photocatalytic performance of Bi₂WO₆ photocatalyst. *Superlattices Microstruct.* 76: 362–375.
- Tabari, T., Singh, D. and Jamali, S.S. (2017). Enhanced photocatalytic activity of mesoporous ZnFe₂O₄ nanoparticles towards gaseous benzene under visible light irradiation. *J. Environ. Chem. Eng.* 5: 931–939.
- Vandenbroucke, A.M., Morent, R., Geyter, N.D. and Leys, C. (2011). Non-thermal plasmas for non-catalytic and catalytic VOC abatement. *J. Hazard. Mater.* 195: 30–54.
- Wang, H., Guo, H., Zhang, N., Chen, Z., Hu, B. and Wang, X. (2019a). Enhanced photoreduction of U (VI) on C₃N₄ by Cr (VI) and bisphenol A: ESR, XPS and EXAFS investigation. *Environ. Sci. Technol.* 53: 6454–6461.
- Wang, H., Li, Q., Zhang, S., Chen, Z., Wang, W., Zhao, G. and Wang, X. (2019b). Visible-light-driven N₂-g-C₃N₄ as a highly stable and efficient photocatalyst for bisphenol A and Cr (VI) removal in binary systems. *Catal Today* 335: 110–116.
- Wang, M., Guo, P., Chai, T., Xie, Y., Han, J., You, M., Wang, Y. and Zhu, T. (2017). Effects of Cu dopants on the structures and photocatalytic performance of cocoon-like Cu-BiVO₄ prepared via ethylene glycol solvothermal method. *J. Alloy. Compd.* 691: 8–14.
- Wang, Y., Long, Y. and Zhang, D. (2016). Novel bifunctional V₂O₅/BiVO₄ nanocomposite materials with enhanced antibacterial activity. *J. Taiwan Inst. Chem. Eng.* 68: 387–395.
- Xia, L., Bai, J., Li, J., Zeng, Q., Li, L. and Zhou, B. (2017). High-performance BiVO₄ photoanodes cocatalyzed with an ultrathin α -Fe₂O₃ layer for photoelectrochemical application. *Appl. Catal. B* 204: 127–133.
- Xiao, H., Qi, C., Cheng, Q., Dou, C., Ning, X. and Ru, Y. (2018). Experimental and modeling studies of SO₃ homogeneous formation in the post-flame region. *Aerosol Air Qual. Res.* 12: 2939–2947.
- Xing, B., Chen, T., Liu, H., Qing, C., Xie, J. and Xie, Q. (2017). Removal of phosphate from aqueous solution by activated siderite ore: Preparation, performance and mechanism. *J. Taiwan Inst. Chem. Eng.* 80: 875–882.
- Yan, X., Sun, Y., Zhu, T. and Fan, X. (2013). Conversion of carbon disulfide in air by non-thermal plasma. *J. Hazard. Mater.* 261: 669–674.
- Yang, C., Gao, G., Guo, Z., Song, L., Chi, J. and Gan, S. (2017b). Two-step hydrothermal synthesis of novel hierarchical Co₃O₄/Bi₂O₂CO₃ *p-n* heterojunction composite photocatalyst with enhanced visible light photocatalytic activity. *Appl. Surf. Sci.* 400: 365–374.
- Yang, F., Wang, Y., Li, H., Yang, M., Li, T., Cao, F., Chen, J. and Wang, Z. (2017a). Influence of cloud/fog on atmospheric VOCs in the free troposphere: A case study at Mount Tai in eastern China. *Aerosol Air Qual. Res.* 10: 2401–2412.
- Yu, Q., Tang, Z.R. and Xu, Y.J. (2014). Synthesis of BiVO₄ nanosheets-graphene composites toward improved visible light photoactivity. *J. Energy Chem.* 23: 564–574.
- Yuan, H., Liu, J., Li, J., Li, Y., Wang, X., Zhang, Y., Jiang, J., Chen, S., Zhao, C. and Qian, D. (2015). Designed

- synthesis of a novel $\text{BiVO}_4\text{-Cu}_2\text{O-TiO}_2$ as an efficient visible-light-responding photocatalyst. *J. Colloid Interface Sci.* 444: 58–66.
- Zhao, J., Lu, Q., Wei, M. and Wang, C. (2015). Synthesis of one-dimensional $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{MoO}_6$ heterostructures by electrospinning process with enhanced photocatalytic activity. *J. Alloys Compd.* 646: 417–424.
- Zhao, W., Wang, Y., Yang, Y., Tang, J. and Yang, Y. (2012). Carbon spheres supported visible-light-driven CuO-BiVO_4 heterojunction: Preparation, characterization, and photocatalytic properties. *Appl. Catal. B* 115: 90–99.
- Zhao, Y., Cui, K., Chen, S., Yin, Z., Chao, H. and Chien, G.P.C. (2018). Atmospheric $\text{PM}_{2.5}$, total PCDD/Fs- WHO_{2005} -TEQ level and wet deposition: Cases of Jinan and Weihai cities, China. *Aerosol Air Qual. Res.* 12: 3081–3095.
- Zhu, C., Lu, J., Wang, X., Qin, H., Li, H. and Wang, J. (2013). Removal of carbon disulfide from gas streams using dielectric barrier discharge plasma coupled with MnO_2 catalysis system. *Plasma Chem. Plasma Process.* 33: 569–579.
- Zou, X., Chen, T., Zhang, P., Chen, D., Liu, H. and Qing, C. (2013). Structural characteristic of natural goethite by thermal treatment. *J. Chin. Ceram. Soc.* 41: 1442–1446.

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