Research Article

Qiuyun Zhang*, Linmin Luo, Yanhui Lei, Feiran Xie, Weihua Li, Yongting Zhao, Jialu Wang, and Yutao Zhang*

Silicotungstic acid supported on Bi-based MOF-derived metal oxide for photodegradation of organic dyes

https://doi.org/10.1515/gps-2023-0193
received September 26, 2023; accepted January 7, 2024

Abstract: In this article, Bi-based metal–organic framework-supported silicotungstic acid (STA) was synthesized by a simple hydrothermal method and used as a precursor for the preparation of the Bi-based MOF-derived catalyst (STA@C-Bi-BDC). Using a combination of FTIR, XRD, SEM-EDS, N₂ adsorption–desorption, TG, UV-Vis DRS, and XPS techniques, the successful immobilization of STA groups on Bi-MOF-derived C-Bi-BDC was assessed. Furthermore, the photocatalytic performance of the as-prepared catalysts was investigated in the degradation of the RhB dye process under visible light. Within 120 min of visible light exposure, the high degradation rate of RhB (92.7%) by STA@C-Bi-BDC system was achieved, which was a lot larger than the STA (39.4%), C-Bi-BDC (59.2%), and STA@Bi-BDC (74.0%) system, and cyclic experiments exhibit that the STA@C-Bi-BDC is a relatively stable photocatalyst. More importantly, the catalyst shows high applicability for the degradation of other dyes. This study reveals a comprehensive strategy for the design of efficient Bi-based MOF-derived photocatalyst for organic dye-based wastewater treatment.

Keywords: silicotungstic acid, bi-based MOF, photocatalysis, dye, photodegradation

1 Introduction

Nowadays, the fast industrialization and civilization process has produced more hazardous pollution to the environment [1,2]. Especially, lots of synthetic dyes (e.g. rhodamine B, acridine orange, neutral red, etc.) have replaced natural dyes and are widely used in many industries such as paper, printing, textile, leather, and so on, and produced a large amount of dye wastewater into the environment [3]. This would not only affect the ecological environment enormously but also have fatal effects on human health [4]. To deal with this dye wastewater, many treatment technologies have been developed, such as physical adsorption techniques, filtration techniques, ozonation techniques, and photocatalytic degradation techniques [5–8]. Among these technologies, photocatalytic degradation has attracted much attention as a water treatment technology due to its simplicity, low energy consumption, low cost, and green non-pollution [9]. However, there exists a challenge regarding the design and construction of effective visible light-responsive photocatalysts during photodegradation.

Currently, a series of photocatalysts have been developed for the degradation of organic dyes, such as TiO₂, ZnO, C₃N₄, CdS, Bi₂WO₆, In₂O₃, heteropolyacids (HPAs), etc. [10,11]. Among them, HPAs (e.g. silicotungstic acid, phosphomolybdic acid) are inorganic metal-oxo clusters with good redox properties and photoinduced charge-transfer properties that can be used as a co-photocatalyst to enhance the photocatalytic [12]. Unfortunately, the photocatalytic of HPAs are limited due to their low surface area and difficult to recycle in polar solvents [13,14]. Then, loading HPAs into supports is one of the most promising routes for heterogeneous photocatalysis.

Metal–organic framework (MOF) has been widely used in many fields due to its high surface area, high porosity, structure variation, and many other outstanding properties [15–17]. Meanwhile, metal oxides derived from MOF have been extensively investigated because they can
maintain the morphological characteristics of original MOF [18]. In recent years, bismuth oxide has been considered a visible light-responsive photocatalytic material, but it is still limited because of its low interfacial area [19]. In this regard, the synthesis of bismuth oxide derived from Bi-based MOF precursors can retain some structural properties of Bi-based MOF and improve optical properties [20]. Until now, no HPAs involving composites based on Bi-based MOF derivatives have been reported.

Herein, the synthesis of STA@Bi-BDC precursor by introducing silicotungstic acid (STA) into the structure of Bi-BDC through a simple hydrothermal route, and subsequent pyrolysis for preparation of the Bi-based MOF-derived catalyst (STA@C-Bi-BDC). Techniques such as FTIR, XRD, SEM-EDS, N2 adsorption–desorption, TG, UV-Vis DRS, and XPS techniques were used to investigate their morphological features and study their optical properties. In addition, the activity of the synthesized composite was assessed through degrading rhodamine B (RhB) under visible light irradiation. Finally, the possible photodegradation mechanism for photocatalytic degradation of RhB was proposed according to the above results.

2 Materials and methods

2.1 Chemical reagents

Bismuth nitrate pentahydrate (Bi(NO3)3·5H2O), terephthalic acid (H2-BDC), silicotungstic acid (STA, H4SiW12O40·nH2O), dimethylformamide (DMF), methanol, rhodamine B (RhB), acridine orange (AO), neutral red (NR), congo red (CR), and methylene blue (MB) were acquired from Sigma-Aldrich. The reagents used in this study were all of analytical grade, and no further purification was needed. In addition, deionized water was used for all of the treatment processes.

2.2 Synthesis of the STA@C-Bi-BDC composite

The STA@Bi-BDC precursor was prepared via a simple one-pot hydrothermal method. In a typical hydrothermal procedure, 0.2492 g H2-BDC was dissolved in 18 mL DMF to form solution A, and 0.4851 g Bi(NO3)3·5H2O was dissolved in 40 mL methanol to form solution B. Then, solution A was added dropwise to solution B under stirring. Subsequently, 0.3 g STA was added in mixture solution by ultrasound for 15 min, and vigorous stirring for 1 h at ambient temperature. The as-obtained mixed solution was transferred to a Teflon stainless autoclave and heated at 150°C for 6 h. After cooling, the obtained precipitate was collected by centrifugation, washed with DMF and water, and dried to obtain the STA@Bi-BDC precursor. To prepare the STA@C-Bi-BDC hybrids, the precursor was calcined at 300°C for 2 h (5°C·min⁻¹) in air atmosphere. Then, cooling to ambient temperature naturally, the as-obtained sample was labeled as STA@C-Bi-BDC. In addition, C-Bi-BDC was prepared based on the same procedures except that no STA was added.

2.3 Characterization techniques

Fourier transform infrared spectra (FTIR) spectra were collected using the T spectrum100 spectrophotometer with KBr pellet. The phase structure of the photocatalysts was identified using the Bruker D8 ADVANCE X-ray diffractometer (XRD, Germany) with Cu Ka radiation source (0.15406 nm). N2 adsorption–desorption analysis was measured using the Micromeritics ASAP 2460 3.01 instrument, and the specific surface area and pore size of the photocatalysts were analyzed using Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods, respectively. Thermogravimetric analysis (TG) was measured on a NETZSCH TG209F1 thermal analyzer under an N2 atmosphere at a heating rate of 10°C·min⁻¹. The UV–visible diffuse reflectance spectroscopy (UV–vis DRS) of the photocatalysts were estimated by a Shimadzu UV-3600 PLUS spectrophotometer (200–800 nm). The chemical states of the elements were examined by X-ray photoelectron spectroscopy (XPS, Thermo Fischer ESCALAB 250XI) with monochromatic Al Ka radiation. The morphologies of the photocatalysts were characterized using a scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS) was employed for the surface species of the prepared photocatalysts.

2.4 Photochemical reactions

The photocatalytic activities of as-prepared catalysts were identified for the decomposition of dyes under visible light in a 300 W xenon arc lamp. Typically, 50 mg catalysts were dispersed in 50 mL, 40 mg·L⁻¹ dye aqueous solutions. Before the photocatalytic reaction, the reaction system was stirred for 30 min in the dark to keep the adsorption–desorption equilibrium of dye molecules and the catalyst. Afterward, the reaction system was exposed to visible light irradiation for 120 min. During the irradiation, approximately 3 mL of
the reaction solution was extracted and centrifuged to remove the catalyst every 30 min until completing 120 min of irradiation. Subsequently, the concentration of dye was measured using UV-5500PC. Finally, the degradation rate $\eta$ is calculated by $\eta = (1 - C_t/C_0) \times 100\%$, where $C_0$ (mg·L$^{-1}$) stands for the initial concentration of dye, and the concentration after irradiation is denoted as $C_t$ (mg·L$^{-1}$).

3 Results and discussion

3.1 Characterization

FTIR spectra of STA, C-Bi-BDC, STA@Bi-BDC, and STA@C-Bi-BDC are presented in Figure 1a. Four absorption peaks were observed in the STA spectrum at 804, 884, 927, and 980 cm$^{-1}$, respectively, indicating the presence of Keggin structure of STA [21]. Compared to the pristine STA, the characteristic absorption peaks of STA are present in the STA@Bi-BDC composite, which essentially indicates the successful introduction of STA on Bi-BDC. However, these characteristic peaks exhibit red-shifted that is an indirect indication of the effect of STA on Bi-BDC. The similarity in band positions of C-Bi-BDC and STA@C-Bi-BDC was observed. However, the peak intensity of the main functional groups of STA@Bi-BDC decreases, which is a direct indication of the effect of pyrolysis on Bi-BDC framework. Surprisingly, no STA characteristic peaks were found in the STA@C-Bi-BDC, illustrating that there is a chemical interaction between STA and Bi-BDC in the pyrolysis process, and the STA is possibly well dispersed on the surface [22]. The FTIR results suggested the successful synthesis of the STA@C-Bi-BDC photocatalyst.

The crystal structure of the catalysts was analyzed using XRD. As illustrated in Figure 1b, the given diffraction peaks of STA were detected at 2$\theta$ values of 7.9°, 9.2°, 16.0°, and 26.5°, consistent with previous reports [23]. As for C-Bi-BDC, the diffraction facets present at 2$\theta$ values of 25.8°, 28.1°, and 33.5° belong to (001), (012), and (022) planes (JCPDS No. 71-0465) [24,25], which indicates that the generation of Bi$_2$O$_3$ phase in the C-Bi-BDC after pyrolysis. With the addition of STA, the peak intensity of the diffraction peak at 2$\theta = 7.9^\circ$ decreased, which confirms the existence of STA in the STA@C-Bi-BDC composite. Besides, a broad diffraction peak at 20–40° was also observed owing to the formation of the amorphous phase, and Bi$_2$O$_3$ peaks were not clearly found. This may be due to the addition of STA affecting the crystal structure of C-Bi-BDC and the existence of a chemical interaction between composite species. In summary, the earlier result suggests the successful preparation of STA@C-Bi-BDC, and the results are consistent with FTIR results.

The morphological features of the C-Bi-BDC and STA@C-Bi-BDC catalysts were probed by SEM images. As displayed in Figure 2a, C-Bi-BDC was an agglomerated irregular block morphology with a smooth surface. After the formation of the composite, it can be clearly seen that the morphologies of STA@C-Bi-BDC were not significantly altered (Figure 2b). However, many small particles are observed on the surface, making its surface relatively rough, thereby indicating that STA has been successfully introduced into STA@C-Bi-BDC composite and the formation of heterojunctions. In addition, the analysis of elemental species was measured using EDS.

Figure 1: (a) FTIR spectra and (b) XRD patterns of the as-prepared catalysts.
(Figure 2c), and the presence of Bi, O, Si, and W species with good dispersion on STA@C-Bi-BDC was confirmed.

Next, N₂ adsorption–desorption experiments were conducted on C-Bi-BDC and STA@C-Bi-BDC catalysts (Figure 3). As can be seen from Figure 3a, both materials can be classified as type-IV adsorption–desorption isotherms with an H3-type hysteresis loop, implying the presence of mesoporous structures, and similar isotherms have also been studied previously [26]. In Figure 3b, the pore size distributions of C-Bi-BDC sample display the mesopores centered at about 3.5 nm, and the STA@C-Bi-BDC sample exhibit the mesopores centered at about 3.8 nm and 10.8 nm, indicating the presence of porous structures within the STA@C-Bi-BDC frameworks. In addition, the physicochemical properties of C-Bi-BDC and STA@C-Bi-BDC catalysts are summarized in Table 1. From Table 1, it can be observed that the \( S_{\text{BET}} \) increases from 6.96 to 14.42 m²·g⁻¹, and the pore volume increases from 0.033 to 0.056 cm³·g⁻¹ for C-Bi-BDC and STA@C-Bi-BDC catalysts, suggesting that the STA was immobilized on the surface of C-Bi-BDC. Notably, the STA@C-Bi-BDC catalyst has a suitable
average pore size. The above data suggest that the mesoporous structure, relatively large \( S_{\text{BET}} \) and wider pore size can expose more active sites and enhance the performance of photocatalysis.

The TG profile of STA@C-Bi-BDC can be divided into two stages, as presented in Figure 4. The first weight loss (1.6%) before 200°C was mainly due to the removal of impurities. Additionally, the second weight loss at the temperature range of 360–550°C could be associated with the thermal decomposition of the STA compounds. Therefore, in this study, the obtained STA@C-Bi-BDC catalyst possessed good chemical stability, and it is beneficial to the improvement of its catalytic activity of photocatalysis.

The optical properties of the STA, C-Bi-BDC, and STA@C-Bi-BDC samples were investigated using the UV–Vis DRS curves. In Figure 5a, it could be seen that all samples exhibited strong light absorption in the range of 200–800 nm, and the maximum absorption band edges of STA and C-Bi-BDC were located at 441 and 471 nm, respectively. Compared with C-Bi-BDC, the light absorption was enhanced in the sample of STA@C-Bi-BDC, and the absorption band edge was extended at 515 nm, suggesting that the loading of STA had an important impact on the optical response range of the STA@C-Bi-BDC composite. According to the Tauc plots, the \( E_g \) corresponding to STA and C-Bi-BDC were 2.97 and 3.19 eV, respectively, whereas the \( E_g \) was 2.81 eV for STA@C-Bi-BDC. It was clear that the presence of STA made the energy band-width of the STA@C-Bi-BDC composite narrower than that of C-Bi-BDC. This meant that the narrow band gap of STA@C-Bi-BDC was conducive to the separation and transition of photogenerated electrons and holes, and further promoted photocatalytic reaction [27].

To study the chemical states of elements in the prepared samples, XPS spectra were employed as shown in Figure 6. In Figure 6a, typical signals of the Bi 4f and O 1s are detected in the spectra of C-Bi-BDC, while the signals assigned to W 4f can be observed in the spectra of STA@C-Bi-BDC, suggesting the successful introduction of STA compounds. In the high-resolution XPS spectra for Bi 4f of C-Bi-BDC (Figure 6a), two peaks located at 159.4 and 164.8 eV were indexed to Bi 4f7/2 and Bi 4f5/2, respectively [28]. However, a certain offset was observed in these peaks of STA@C-Bi-BDC, implying a partial electron transfer from C-Bi-BDC frameworks to the STA cluster according to strong metal-support interactions [29,30], which is consistent with XRD analysis. As depicted in Figure 6c, for C-Bi-BDC, two peaks at 530.0 and 531.4 eV are matched to the Bi-O bonds in the Bi2O3 and the presence of the O–H bond in the sample's surface [31]. Interestingly, the new peak of the STA@C-Bi-BDC sample at 530.6 eV was caused by the presence of the W–O bond [23]. Figure 6d exhibits the W 4f spectra, which could be deconvoluted into two characteristic peaks, and the peaks at 35.6 and 37.8 eV belonged to the W 4f7/2 and W 4f5/2, respectively, indicating the presence of W⁶⁺ in the STA@C-Bi-BDC sample, consistent with many reports [32]. Overall, the above results further proved the successful preparation of the STA@C-Bi-BDC photocatalyst and are accordant with FTIR and XRD results.

### 3.2 Photocatalytic activity of as-synthesized catalysts

Photocatalytic performance of the as-synthesized catalysts was investigated via the degradation of RhB under visible light. As can be seen in Figure 7a, the results of the blank experiment show that RhB cannot spontaneously be degraded under visible light. After 120 min of visible light irradiation, the degradation rate of RhB by STA, C-Bi-BDC, and STA@C-Bi-BDC is 39.4%, 59.2%, and 74.0%, respectively. Excitingly, the prepared STA@C-Bi-BDC exhibits remarkably enhanced photocatalytic activity after the pyrolysis of STA@C-Bi-BDC. In addition, the reaction kinetic profile for the degradation of RhB and the corresponding apparent rate constants by different catalysts was also explored (Figure 7b and c). It can be seen that the apparent rate constant \((k)\) for the STA@C-Bi-

---

**Table 1: Textural parameters of C-Bi-BDC and STA@C-Bi-BDC catalysts**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-Bi-BDC</td>
<td>6.96</td>
<td>0.033</td>
<td>12.6</td>
</tr>
<tr>
<td>2</td>
<td>STA@C-Bi-BDC</td>
<td>14.42</td>
<td>0.056</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Figure 4: TG Profile of STA@C-Bi-BDC.**
Figure 5: (a) The absorbance of the UV–Vis diffuse reflectance spectra and (b) Tauc plot for STA, C-Bi-BDC, and STA@C-Bi-BDC samples.

Figure 6: (a) Full XPS survey spectra, (b) Bi 4f, (c) O 1s spectra of C-Bi-BDC and STA@C-Bi-BDC, and (d) W 4f spectra of STA@C-Bi-BDC.
BDC is approximately 5.2 times that of STA, 2.8 times that of C-Bi-BDC, and 2.0 times that of STA@Bi-BDC, respectively. Therefore, the best photocatalytic performance was achieved by STA@C-Bi-BDC. This is possible owing to its mesoporous structures, relatively large $S_{\text{BET}}$, wider pore size, narrow bandgap energy, and the presence of heterojunction structure, which improves the separation of photoexcited electron–hole pairs [33]. Besides, Figure 7d presents the absorption spectrum change of RhB photo-degraded by STA@C-Bi-BDC. The results clearly demonstrate that the rapid decrease of the peak intensity of RhB at 554 nm and the characteristic peak wavelength gradually shifts to blue as the light exposure time is increased. Meanwhile, the discoloration of absorbance is because of the N-de-ethylation of RhB, confirming the degradation of RhB [34].

3.3 Effects of several parameters on the photodegradation of RhB

The effect of catalyst and dye concentration on STA@C-Bi-BDC for RhB degradation was investigated and summarized in Figure 8a and b. From Figure 8a, it is clear that the degradation rate of RhB enhances with increasing the concentration of catalyst, signifying the presence of more active sites on the catalyst surface by increasing catalyst concentration. Further, up to 1.2 g·L\(^{-1}\) concentration of STA@C-Bi-BDC, there was no significant increase in the degradation rate of RhB. Thus, the catalyst concentration is chosen as 1.0 g·L\(^{-1}\) for further studies. As shown in Figure 8b, the degradation rate decreased with increasing RhB concentration, and this is due to the fact that a large amount of adsorbed RhB dye may inhibit reactions.
Figure 8: (a) Effect of catalyst dosage, (b) initial RhB concentration, and (c) recyclability of STA@C-Bi-BDC in degradation of RhB under visible light irradiation, (d) XRD and (e) FTIR patterns of STA@C-Bi-BDC before and after the reaction, and (f) the photocatalytic degradation rates for different dyes by STA@C-Bi-BDC (1.0 g·L⁻¹).
between RhB molecules and free radicals [35]. However, the degradation rate for 30 and 40 mg·L\(^{-1}\) of RhB concentration was not noticeably changed in 120 min. Therefore, in the following experiments, 40 mg·L\(^{-1}\) was selected as the initial RhB concentration for photodegradation.

### 3.4 Photocatalyst recycling

The reusability of the catalyst is an important parameter for real‐field applications. To test the reusability of STA@C-Bi-BDC, the recycling experiment for degradation of RhB has been performed three times under the same conditions. After each cycle, the catalyst was recycled by centrifuging, washing, and drying for the next cycle of the experiment. As shown in Figure 8c, the degradation rate of RhB photodegradation still reached 77.0% after three cycles. Moreover, we also tested the XRD and FTIR patterns of the catalyst after three cycles. According to Figure 8d, the diffraction peak of the recycled STA@C-Bi-BDC at 7.9° was not clearly found, and some miscellaneous peaks were observed; this is possible because of the existence of STA leaching and the adsorption of dyes and intermediates onto the surface and pores of the catalyst. Additionally, from Figure 8e, there is no obvious difference between FTIR spectrums of fresh and used catalysts, suggesting that the basic structure of the catalyst almost remains intact after repeated utilization. The results above indicate that the STA@C-Bi-BDC is a relatively stable photocatalyst.

### 3.5 Photocatalytic degradation of various dyes

Figure 8f shows the degradation of other dyes in the STA@C-Bi-BDC system under visible light irradiation. It can be seen that the degradation rates of CR, AO, and NR in STA@C-Bi-BDC system were 86.3%, 95.9%, and 91.4% after 120 min, respectively. Obviously, the STA@C-Bi-BDC exhibits a high photocatalytic performance for all dyes, suggesting the excellent generality of as-obtained STA@C-Bi-BDC hybrids.

### 3.6 Possible photocatalytic mechanisms

According to the literature, the possible reaction mechanism of RhB photodegradation over STA@C-Bi-BDC is proposed in Figure 9. The forbidden bandwidth of STA@C-Bi-BDC is 2.81 eV (Figure 5), lower than that of C-Bi-BDC (3.19 eV). This may be due to an intermediate energy level being induced in the bandgap region of C-Bi-BDC after the introduction of STA, and allowing electrons to move towards it, making the bandgap smaller [36]. When visible light irradiates the catalyst surface, the electrons in the valence band (VB) of STA@C-Bi-BDC are excited to the conduction band (CB), leaving behind the holes in the VB, producing electron–hole pairs. The photogenerated holes behave as an oxidizing agent that reacts with water molecules to produce hydroxyl (·OH) radicals. Meanwhile, the dissolved oxygen can be reduced by electrons to form ‘O\(_2\)\(^{-}\) radicals [37]. At last, the generation of ‘OH and ‘O\(_2\)\(^{-}\) radicals can be used as active species for synergistic degradation of RhB into green products.

### 4 Conclusion

In conclusion, the STA@C-Bi-BDC catalyst was successfully synthesized and constructed by a simple one-pot hydrothermal method and following the pyrolysis process, and
the photocatalytic activity of the catalyst was evaluated for the degradation of RhB. As a result, STA@C-Bi-BDC showed a maximum degradation performance of up to 92.7% for RhB, much higher than that of STA@Bi-BDC (74.0%), C-Bi-BDC (59.2%), and pristine STA (39.4%) in 120 min under visible irradiation. The excellent photocatalytic activity was attributed to its mesoporous structures, relatively large \( S_\text{BET} \), strong light absorption, and excellent charge transfer behavior. Furthermore, the STA@C-Bi-BDC catalyst demonstrated relatively good stability and generality. This work offers a promising approach to constructing a Bi-based MOF-derived catalyst for organic dye-based wastewater treatment.

**Funding information:** This work was financially supported by the Porous Materials and Green Catalysis Innovation Team in High Education Institute of Guizhou Province (Qianjiaojing[2023]086), the Key Laboratory of Agricultural Resources and Environment in High Education Institute of Guizhou Province (Qianjiaojing[2023]025), the Scientific Research Back Feeding Teaching Special Project of Anshun University (asxykyb202306), the Anshun Science and Technology Planning Project (Anshikeping[2020]02), and the innovative entrepreneurship training program for undergraduates of the Guizhou education department (202310667004, 202310667005).

**Author contributions:** Qiuyun Zhang: writing-original draft, writing-review & editing, methodology, formal analysis, and project administration; Linmin Luo: methodology and formal analysis; Yanhui Lei: writing-review & editing; Feiran Xie: methodology and formal analysis; Weihua Li: formal analysis; Yongting Zhao: visualization; Jialu Wang: visualization; Yutao Zhang: visualization and project administration.

**Conflict of interest:** The authors state no conflict of interest.

**Data availability statement:** All data generated or analyzed during this study are included in this published article.

**References**


