Carbon-doped flower-like Bi2WO6 decorated carbon nanosphere nanocomposites with enhanced visible light photocatalytic degradation of tetracycline

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Abstract

In search of a recyclable catalyst with synergistic adsorption and photocatalysis, unique composite photocatalysts of flower-like bismuth tungstate (Bi$_2$WO$_6$) and carbon nanospheres (CSs) were synthesized using a hydrothermal synthesis method (named CSs-Bi$_2$WO$_6$). Based on the large specific surface area and a reasonable band gap (2.53 eV), CSs-Bi$_2$WO$_6$ have good photocatalytic properties. For example, the composite with an optimized ratio (2 wt% CSs-Bi$_2$WO$_6$) showed good adsorption and photocatalytic performance. Under visible light irradiation, the photodegradation rate of tetracycline (TC) by adding 2% CSs is 25% higher than that of pure Bi$_2$WO$_6$. After five cycles, the observed barely decreased TC degradation rate of 2% CSs-Bi$_2$WO$_6$ confirmed the high cyclability and reproducibility of the photocatalyst. The CSs greatly improved the adsorption of pollutants and reduced the recombination rate of photogenerated electrons and holes of the Bi$_2$WO$_6$. This study provides a promising new method for the efficient removal of organic pollutants.

1. Introduction

With the rapid development of the social economy, environmental pollution has brought serious and inevitable problems to human society [1]. Therefore, environmental remediation is one of the key issues of human sustainable development. The polluted water seeps into the ground, which further leads to different degrees of pollution of soil and groundwater [2, 3]. Antibiotics have been widely used in the last decades for controlling human and animal diseases. Tetracycline (TC) ranks second on the global list of antibiotic production and consumption due to its high efficacy against a variety of pathogenic bacteria [4]. TC can exist for a long time in an environment tends to increase the antibiotic resistance of the receiving body, disrupts ecological stability, and threatens subsequently human health [5, 6]. Consequently, it is critical to develop efficient and cost-effective methods for the control of TC in the environment.

Among many methods of sewage treatment, adsorption has been regarded as one of the most effective options for treating pollutants in water owing to its low cost and high efficiency [7]. We note that carbon materials are attracting more and more attention in the application of adsorption, drug delivery, as well as catalysis [8, 9]. In particular, carbon nanosphere (CS) can provide a high specific surface area and faster molecular diffusion/transfer [10]. In addition, the carbon component can effectively enhance the absorption of visible light and form a strong interface electronic effect with the semiconductor [11, 12]. They can be used as the main carrier of photocatalyst and have attracted extensive attention.

Nevertheless, in the adsorption process, CSs can only absorb organic pollutants rather than degrade them into nonpolluting matters, which will result in secondary pollution and limit their application [13, 14]. To resolve the above problems, a synergetic strategy of combining adsorption with photocatalysis has been developed, in which organic pollutants can be firstly adsorbed and enriched, and then decomposed and mineralized via a photocatalytic process [15, 16].
Semiconductor-based photocatalysis has been recognized as a promising technology for energy conversion, environmental remediation, organic pollution disposal and selective oxidation [17, 18]. Many Bi-based photocatalysts have been modified by the carbonaceous materials [19, 20]. Bi$_2$WO$_6$ is one of the semiconductor materials with environmental protection, high light stability, and nontoxicity. Due to its special sandwiches-like layered structure of [Bi$_2$O$_2$]$^{2+}$ and [WO$_6$]$^{2-}$, Bi$_2$WO$_6$ has a better chemical property and stability than monolayer catalysts like CuO and CoS$_2$[21]. The hybrid of Bi 6s and O 2 p orbit formed the valence band of Bi$_2$WO$_6$, and the W 5 d orbit composed the conduction band at the same time [22–24]. It has an appropriate band gap value (2.75 eV) and thus visible light responses [25]. It is becoming one of the most promising photocatalysts in recent years. However, due to the fast recombination rate of photogenerated electrons and holes, the application of pure Bi$_2$WO$_6$ photocatalyst is greatly limited [26].

In this report, we prepared composite structures of homogeneously dispersed CSs with flower-like Bi$_2$WO$_6$ by a hydrothermal synthesis method. This method makes full use of the high absorption properties of carbon materials and the photo-responsive of semiconductor materials and has a wide range of applications in environmental remediation.

2 Experiment Section

2.1 Chemicals and Characterization

Detailed information on experimental reagents and apparatus was provided in the supporting information.

2.2 Preparation of CSs

In a typical process [27], 4 g of D-(+)-Glucose was added to 30 mL of deionized H$_2$O. Then the mixture was transferred into a 50 mL Teflon-lined steel autoclave and heated to 180 °C for a period of 8 h. The obtained black-brown carbonaceous materials were washed three times with water and ethanol, respectively. The material was dried in an oven at 80 °C.

2.3 Preparation of CSs-Bi$_2$WO$_6$

Bi$_2$WO$_6$ was prepared according to the hydrothermal procedure as described elsewhere [28]. In short, about 0.5 mol of Bi(NO$_3$)$_3$ 5H$_2$O and 0.5 mol Na$_2$WO$_4$ 2H$_2$O were dissolved in 25 mL of ethylene glycol and stirred to produce a white precipitate. A certain amount of CSs was dissolved in 10 mL distilled water by ultrasound, which was then added dropwise to the above solution. It was then transferred to a Teflon-lined stainless steel autoclave, which was heated at 140 °C for 14 hours, and then naturally cooled down to ambient temperature. The samples obtained were washed three times with ethanol and deionized water respectively and then centrifuged. The repeatedly washed sediment was dried at 60 °C. The composite catalysts with different CSs contents were labeled as Bi$_2$WO$_6$, 0.5% CSs-Bi$_2$WO$_6$, 1% CSs-Bi$_2$WO$_6$, 2% CSs-Bi$_2$WO$_6$, 4% CSs-Bi$_2$WO$_6$, 8% CSs-Bi$_2$WO$_6$. 
2.4 Photocatalytic TC degradation

Photodegradation of TC was used to evaluate the photocatalytic activity of CSs-Bi$_2$WO$_6$, a 300-W xenon lamp ($\lambda \geq 420$ nm) was used for irradiation and TC solution was used as a model substrate. Briefly, 50 mg of the prepared photocatalyst was added to 100 mL TC solution (50 mg/L). Before light irradiation, it was stirred for 30 min in the dark to reach adsorption equilibrium. After a certain time interval, 3 mL suspension was extracted and centrifuged to obtain a clarified solution. The absorbance of TC solution was measured at 358 nm using a UV-visible spectrophotometer. Control experiments were performed with a single Bi$_2$WO$_6$. The degradation percent and apparent rate constant are calculated by Eqs. (1) and (2), respectively:

\[
\text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)
\]

\[
\ln \left( \frac{C_0}{C_t} \right) = kt \quad (2)
\]

where \(C_0\) is the initial concentration of TC solution, and \(C_t\) is the concentration of TC solution at time \(t\).

\[
\ln \left( \frac{C_0}{C_t} \right)
\]

has a linear relationship with \(t\), and \(k\) is the apparent rate constant (min$^{-1}$).

2.5 Adsorption kinetics study

Details of adsorption kinetics are provided in the supporting information.

3 Results And Discussion

The morphology of Bi$_2$WO$_6$ (Fig. 1a) was assembled by numerous nanosheets, which intercrossed each other and aggregated together, forming the flower-like microstructure with a diameter of 3–4 $\mu$m. As seen from Fig. 1b, CSs and Bi$_2$WO$_6$ were attached to each other. However, CSs were unevenly distributed on the surface of Bi$_2$WO$_6$ and the ends were more likely to be covered $[29]$. The main reason for this phenomenon was probably owing to the stacking of Bi$_2$WO$_6$ sheets in flower shape and the uneven distribution of the stress on the surface. The structure and morphology of the as-prepared CSs are displayed in Fig. 1c, from which we can see clearly that the shape of CSs was uniform and well-dispersed spheres with more regular structures and smooth surfaces, and the average diameters of the CSs was about 450 nm. The surface of CSs in Fig. 1b changed from smooth to rough, which may be affected by the growth of Bi$_2$WO$_6$ $[30]$. It could not prevent the CSs from forming close contact with Bi$_2$WO$_6$ to form a ‘flower-spheres’ structure, and will even be more conducive to the surface adsorption of organic pollutants. However, if the content of CSs increases, it is easy to form large clusters. This will affect the
interaction between CSs and Bi$_2$WO$_6$. The EDS results in Fig. 1d-1g demonstrate the distribution of C, O, W, and Bi elements in the CSs/Bi$_2$WO$_6$ composites, indicating the successful production of the composite catalysts.

In Fig. 1h, it can be seen that the 2% CSs-Bi$_2$WO$_6$ composite structure exhibits the ‘flower-spheres’ morphology. The layered structure of Bi$_2$WO$_6$ can be clearly seen in the picture as consisting of a large number of nanosheets. The CSs are attached to the nanosheets. Further, The lattice spacings measured in HRTEM image (Fig. 1i) were approximately 0.27 nm and 0.32 nm, corresponding to the (200) and (131) crystal faces of Bi$_2$WO$_6$ [31]. The isotherm curves of Bi$_2$WO$_6$ belonged to type IV with H3 hysteresis loops, corresponding to slit-shaped pores consistent with the sheet-like morphology (displayed in Fig. 3) [32]. In Fig. 1j, we can still find the (020) and (131) crystal faces of Bi$_2$WO$_6$ clearly in the 2% CSs-Bi$_2$WO$_6$ catalyst.

The XRD patterns showed the phase structure of the CSs-Bi$_2$WO$_6$ complexes in different proportions (Fig. 2a). The characteristic diffraction peaks appeared at 2θ = 28.30°, 32.79°, 47.15°, 55.83°, 58.55°, 75.96°, and 78.35°, which were well-matched with the crystal planes (113), (200), (220), (313), (226), (139), and (420) of Bi$_2$WO$_6$ standard card (PDF#26-1044), demonstrating the successful preparation of Bi$_2$WO$_6$ [33, 34]. There were no other reflections associated of carbon phases in any with the XRD patterns of the composites. This was somehow expected due to the low amount of carbon additive used in the preparation of the composites and their high dispersion in samples.

The chemical states of Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ were investigated by XPS analysis, and the results were shown in Fig. 2b-2d. From Fig. 2b, the presence of elements such as C, O, Bi, and W was clearly observed. Figure 2c shows the XPS spectra of C 1 s peak for pure Bi$_2$WO$_6$. and 2% CSs-Bi$_2$WO$_6$. The C 1 s peaks at around 284.6 eV and 288.3 eV were attributed to the carbon signal from carbon in the instrument for calibration and the adsorbed CO$_2$ on the surface respectively [35]. It was worth noting that there was a new peak at 286.2 eV for 2% CSs-Bi$_2$WO$_6$, which could be ascribed to the formation of C - O - C (the O atoms in Bi$_2$WO$_6$) between Bi$_2$WO$_6$ and CSs. The above result indicated that most of C in 2% CSs-Bi$_2$WO$_6$ was sp$^2$ hybridized. The presence of oxygen-containing functional groups such as C = O, C - O and C - O - C in the 2% CSs-Bi$_2$WO$_6$ system suggests that the strong interaction between Bi$_2$WO$_6$ and carbon nanospheres is formed during the hydrothermal reaction.

O 1 s spectra for the samples of pure Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ are shown in Fig. 2d. The asymmetric peak centered at 530 eV was decomposed into two components at the binding energy of 529.74 eV and 531.33 eV for pure Bi$_2$WO$_6$, which were due to the surface lattice oxygen and the adsorbed oxygen species respectively [36, 37]. With the addition of the CSs, the oxygen peak becomes complex. The binding energy shifts from 529.75 eV, 531.33 eV (Bi$_2$WO$_6$) to 531.08 eV, 527.68 eV (2% CSs-Bi$_2$WO$_6$). The decrease in binding energy indicated the presence of complex oxygen groups in the composite. The electron cloud density and electronegativity around O decrease due to the addition of carbon spheres.
The BET and the pore structure of the prepared samples are shown in Fig. 3. The isotherm curves belonged to type IV with H3 hysteresis loops [32], which corresponds to slit-like pores, consistent with the morphology of the flakes as shown in the SEM.

In Fig. 3a, specific surface area of pure Bi$_2$WO$_6$, 0.5% CSs-Bi$_2$WO$_6$, 1% CSs-Bi$_2$WO$_6$, 2% CSs-Bi$_2$WO$_6$, 4% CSs-Bi$_2$WO$_6$, and 8% CSs-Bi$_2$WO$_6$ was 20.76, 86.34, 87.57, 88.05 87.04 and 85.92 m$^2$ g$^{-1}$, respectively. As mentioned earlier, the growth of Bi$_2$WO$_6$ affects the surface morphology of the CSs. On one hand, the addition of surface area was mainly caused by the surface folds of CSs, which will increase the contact area of CSs with contaminants. On the other hand, the pore size and total pore volume of the sample increased somewhat compared to that of pure Bi$_2$WO$_6$, and the value of 2% CSs-Bi$_2$WO$_6$ reached its maximum. This proves that adsorption is strongly related to the specific surface area of the composite catalyst. The pore size distribution is shown in Fig. 3b, which indicated that the major pore sizes were in the range from 2 to 10 nm, belonging to mesopore scope.

Photoluminescence (PL) is regarded as a powerful tool to study the efficiency of electron-hole pair separation. The PL spectra clearly showed the strong emission peaks of the samples at 425 nm under excitation at 378 nm. Figure 4a shows that the emission intensity of CSs-Bi$_2$WO$_6$ was lower than that of pure Bi$_2$WO$_6$. In particular, the 2% CSs-Bi$_2$WO$_6$ showed the lowest emission intensity. This trend suggested that the separation efficiency of photogenerated electrons and holes can be effectively improved by introducing CSs, which in turn promoted the enhancement of photocatalytic activity.

Figure 4. PL spectra for CSs-Bi$_2$WO$_6$ (a), Mott-Schottky curve of Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ (b), Transient photocurrent response of CSs-Bi$_2$WO$_6$ (c), electrochemical impedance spectroscopy (EIS) measurements of Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ (d).

In Fig. 4b the x-intercept of the linear region was used to calculate the flat-band potential, and the obtained results are converted into NHE potentials to further calculate the E$_{CB}$ for Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ Schottky contacts [40–42]. The straight upward curves demonstrated that Bi$_2$WO$_6$ was a n-type semiconductor. The flat-band potentials of both the Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ composites was −0.46 V vs. Ag/AgCl (−0.26 eV vs. NHE (normal hydrogen electrode)), respectively. The E$_{CB}$ for both the Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ Schottky contacts was approximate − 0.36 eV. Combined with the band gap values obtained from Tauc plots, the valence band potentials (VB) of 2% CSs-Bi$_2$WO$_6$ samples was calculated to be 2.17 eV [43].

The photocurrent responses of the pure Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ were tested and the results are displayed in Fig. 4c. It can be found that both of the photoelectrodes exhibit stable photocurrent responses over several on-off cycles. When the photoelectrodes were exposed to the light, photocurrents were generated immediately for all the samples. Obviously, Bi$_2$WO$_6$ had the lower photocurrent responses due to the higher recombination rate of photogenerated electrons and holes in the Bi$_2$WO$_6$ crystal. The photocurrent response of the composite photocatalyst 2% CSs-Bi$_2$WO$_6$ was about 9 times higher than
pure Bi$_2$WO$_6$, which effectively indicated more efficient photo-induced charge separation and faster electron transport. The EIS Nyquist plots for Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ under dark and light conditions are shown in Fig. 4d, respectively. The graph clearly showed that the arc radius of 2% CSs-Bi$_2$WO$_6$ was smaller than Bi$_2$WO$_6$, indicated that the introduction of CSs enhanced the charge migration of Bi$_2$WO$_6$ and reduces the reaction resistance at the semiconductor interface. Furthermore, the arc radiation of Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ was smaller under light than under dark conditions, indicated that more carriers were generated due to the excitation of light.

In order to test the photocatalytic property, TC was chosen as the target pollutants. To study the TC degradation kinetics in the presence of CSs-Bi$_2$WO$_6$, the apparent reaction rate constant ($k$) was calculated by using the first-order reaction model as shown by Eq. (3) [44]:

$$\ln\left(\frac{C}{C_0}\right) = -kt(3)$$

where $C_0$ and $C$ are the concentration of TC at time 0 and $t$ min respectively. The normalized reaction rate constant was calculated by normalizing $k$ with the total mass of catalysts. The photodegradation result of TC is shown in Fig. 6. Under visible light, 50 mg photocatalyst was added to 100 mL 50 mg/L TC solution for photocatalytic degradation. The experimental results showed that 2% CSs-Bi$_2$WO$_6$ has the best photocatalytic degradation performance for TC.

Figure 5a is a diagram of the degradation rate of TC by the catalyst. The composite photocatalyst reached adsorption-desorption equilibrium within 40 minutes of the dark reaction (detailed data of adsorption in support information). The degradation rate of TC by 2% CSs-Bi$_2$WO$_6$ was 84.6%, which is nearly 25% higher than pure Bi$_2$WO$_6$. This was because 2% CSs-Bi$_2$WO$_6$ had a large specific surface area, especially the folded structure of CSs, which effectively increased the adsorption of TC by the catalyst and promoted the photoreaction. In addition, the carbon component can effectively enhance the absorption of visible light and form a strong interface electronic effect with the semiconductor. Compared with the work reported in the literature on degradation of organic pollutants by carbon materials in Table S2.

In Fig. 5b, the degradation kinetics had a linear relationship between $\ln\left(\frac{C_0}{C_t}\right)$ and irradiation time, which shows that the catalyst follows the pseudo-first order kinetics. The rate constant in the equation was calculated from the slope $k$ of the kinetic curve. The rate constants for pure Bi$_2$WO$_6$, 0.5% CSs-Bi$_2$WO$_6$, 1% CSs-Bi$_2$WO$_6$, 2% CSs-Bi$_2$WO$_6$, 4% CSs-Bi$_2$WO$_6$, and the 8% CSs-Bi$_2$WO$_6$ were 0.01502 min$^{-1}$, 0.00257 min$^{-1}$, 0.02141 min$^{-1}$, 0.03929 min$^{-1}$, 0.02951 min$^{-1}$ and 0.0703 min$^{-1}$, respectively. In particular, 2% CSs-Bi$_2$WO$_6$ had the highest photocatalytic degradation rate, which should be attributed to more efficient charge separation by the adding CSs. The stability and reproducibility of photocatalysts are of great research value in practical applications. Figure 5c shows the photocatalytic cycling test plots of the
prepared catalyst samples. After the 5th cycle, the final degradation rate was about 80.5%, which displayed a better photocatalytic stability of 2% CSs-Bi$_2$WO$_6$.

The main active species of different photocatalysts may differ due to their different energy band structures. In the present study: dimethyl sulfoxide (DMSO), ammonium oxalate (AMO), isopropyl alcohol (IPA) and 1,4-benzoquinone (BQ) were used as electron (e$^-$), hole (h$^+$), hydroxyl radical (·OH$^-$) and superoxide radical (·O$_2^-$) scavengers, respectively [45]. The photocatalytic degradation of TC was carried out with different scavengers under visible light irradiation and the results are shown in Fig. 5d. The presence of BQ and AMO significantly inhibited the photodegradation of TC, indicated that ·O$_2^-$ and h$^+$ were the main active species (results were consistent with ESR in supporting information). Photodegradation was also somewhat inhibited when DMSO was added into the system, indicating that the e$^-$ are more active in the composite photocatalyst. In addition, the addition of IPA had little effect on the photocatalytic performance. Therefore, the order of role of the active species in the 2% CSs-Bi$_2$WO$_6$ photocatalytic degradation TC was ·O$_2^-$ > h$^+$ > e$^-$ > ·OH$^-$.

Based on the above results, a schematic representation of the photocatalytic degradation mechanism of 2% CSs-Bi$_2$WO$_6$ under visible light irradiation is given in Fig. 6. It was generally accepted that, after photoillumination, the generation of the electron and hole in CB and VB is expected, respectively. According to Fig. 5b, the CB of 2% CSs-Bi$_2$WO$_6$ was −0.36 eV vs. NHE, which was more negative than the redox potential ($E_{O_2/O_2^-}$ = −0.33 eV vs. NHE). Thus, the photogenerated electrons were transferred to O$_2$, which was transformed to produce ·O$_2^-$. In addition, combined with the band gap energy ($E_g$) of 2% CSs-Bi$_2$WO$_6$, the VB potential of 2% CSs-Bi$_2$WO$_6$ can be calculated as +2.17 eV vs. NHE according to the formula (CB = VB - $E_g$) [46]. Specific data are described in the supporting information. The VB level of 2% CSs-Bi$_2$WO$_6$ was lower than $E_{\text{\text{\textipa{H}/\textipa{H}}}^{-}}$ = +2.31 V vs. NHE. Therefore, ·OH$^-$ did not play a major role in the photocatalytic reaction, which is in agreement with Fig. 6.

Upon visible light irradiation of the semiconductor, the electron-hole pairs were generated. The photogenerated electrons reacted with O$_2$ (from the air) on the photocatalyst surface to form the ·O$_2^-$, which finally can be converted to ·OH$^-$·. In addition, the photogenerated holes in the VB of the photocatalyst could also oxidize the TC [27, 47]. To sum up, the 2% CSs-Bi$_2$WO$_6$ photocatalyst exhibited a greater electron-hole separation efficiency, compared to the bare Bi$_2$WO$_6$ photocatalyst. It should be noted that the photodegradation mechanism of the TC was proposed as Equations (4–8):

\[
Bi_2WO_6 + hv \rightarrow Bi_2WO_6 + e^- + h^+ (4)
\]

\[
e^- + O_2 \rightarrow \cdot O_2^- (5)
\]

\[
\cdot O_2^- + 2H_2O + e^- \rightarrow 4 \cdot OH^- (6)
\]
\[ \cdot O_2^- + TC \rightarrow \text{products}(7) \]
\[ h^+ + TC \rightarrow \text{products}(8) \]

During the dark reaction, TC was adsorbed on the surface of CSs due to irregular folds on the surface and strong adsorption. It facilitated the transfer of pollutants from the environment to the surface of the catalyst, forming a high concentration TC environment on the surface. And finally adsorption - dissolution equilibrium was achieved. In addition, CSs have a good electrical conductivity, which is conducive to the separation of photogenerated electrons and holes, and prolongs the life of carriers, thus improving the photocatalytic performance.

4 Conclusion

In summary, the composite photocatalyst of CSs-Bi$_2$WO$_6$ was synthesized by a simple hydrothermal method and applied to the photocatalytic degradation of organic pollutants. In the composite catalyst, TC in water formed a highly concentrated TC environment on the surface of CSs due to their strong adsorption. The TC molecules then gradually diffuse to the surface of Bi$_2$WO$_6$ so that the composite photocatalyst and the pollutant eventually reach an adsorption-dissolution equilibrium. The composite photocatalyst has excellent photocatalytic degradation effect on TC and other organic compounds. It opens up a new vision for the synergistic effect of carbon and semiconductor materials in the field of environmental remediation.

Declarations

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Author Contributions Statement

Xiaona Jiang, Xinrui Zhang and Houjuan Qi wrote the main manuscript text and Shuai Chen and Lanni Qu prepared figures. All authors reviewed the manuscript.

Declaration of Competing Interest

There are no conflicts to declare.

References


Fe$_3$O$_4$/Bi$_2$WO$_6$ composites. ACS omega 6:1647–1656. https://doi.org/10.1021/acsomega.0c05616


**Figures**

![Figure 1](image)

**Figure 1**

SEM images of Bi$_2$WO$_6$ (a), 2% CSs-Bi$_2$WO$_6$ (b), CSs (c), the element distribution of C, O, Bi, and W in 2% CSs-Bi$_2$WO$_6$ (d-g), TEM images of 2% CSs-Bi$_2$WO$_6$ (h), and HRTEM images (i, j) of Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$. 
Figure 2

XRD patterns of Bi$_2$WO$_6$ and CSs-Bi$_2$WO$_6$ photocatalysts (a), XPS spectra of the Bi$_2$WO$_6$ and 2% CSs-Bi$_2$WO$_6$ (b), C 1s spectra (c), O 1s spectra (d).

Figure 3

N$_2$ adsorption-desorption isotherms and pore size distribution curves (the inset) of Bi$_2$WO$_6$ and CSs-Bi$_2$WO$_6$. 
Figure 4

PL spectra for CSs-Bi₂WO₆ (a), Mott-Schottky curve of Bi₂WO₆ and 2% CSs-Bi₂WO₆ (b), Transient photocurrent response of CSs-Bi₂WO₆ (c), electrochemical impedance spectroscopy (EIS) measurements of Bi₂WO₆ and 2% CSs-Bi₂WO₆ (d).
Figure 5

Variation of TC concentration with irradiation time on synthesized samples under visible light irradiation. (The experiment was repeated three times) (a), first-order kinetic curves of photocatalytic TC degradation in the as-synthesized samples (b), reusability of 2% CSs-Bi$_2$WO$_6$ in five runs for TC (c), mapping of active species captured in the TC photodegradation system on 2% CSs-Bi$_2$WO$_6$ under visible light (d).
Figure 6

Possible mechanism of TC on the surface of 2% CSs-Bi$_2$WO$_6$ composite.

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