Synthesis and Broadband Spectra Photocatalytic Properties of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$

Junping Ding$^{1,2}$, Huanchun Wang$^{1,3}$, Haomin Xu$^1$, Lina Qiao$^1$, Yidong Luo$^1$, Yuanhua Lin$^{1,*}$ and Cewen Nan$^1$

$^1$ State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China; dpi5@mails.tsinghua.edu.cn (J.D.); huanchwang@163.com (H.W.); xuhm13@mails.tsinghua.edu.cn (H.X.); qln13@mails.tsinghua.edu.cn (L.Q.); ydluozd@163.com (Y.L.); cwnan@mail.tsinghua.edu.cn (C.N.)

$^2$ China Astronaut Research and Training Center, Beijing 100094, China

$^3$ High-Tech Institute of Xi’an, Xi’an 710025, China

* Correspondence: linyh@mail.tsinghua.edu.cn; Tel.: +86-10-6277-3741

Received: 31 March 2018; Accepted: 3 May 2018; Published: 14 May 2018

Abstract: High efficiency photocatalyst Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ was synthesized conveniently with chemical bath precipitation using Bi$_2$O$_2$CO$_3$ as the precursor. The microstructures of the samples are systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and UV-Vis spectroscopy; the optical and photocatalytic properties are carefully tested as well. The content of S, which was tuned through the controlling of the precipitation process, was verified to have an intense effect over the photocatalytic properties. A nearly saturated S ratio and the best photocatalytic performance were observed in specimens with the most S content. Our study reveals that, with negligible influence of the morphology and crystal structure, Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ possessed a broadened optical absorption region from ultraviolet to visible light, and enhanced photocatalytic activity in comparison to precursor Bi$_2$O$_2$CO$_3$ in photocatalytic degradation of Congo Red aqueous solution.

Keywords: Bi$_2$O$_2$CO$_3$; Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$; broadband spectra; photocatalysis

1. Introduction

Semiconductor photocatalysis has attracted increasing attention because of the capability of harvesting the solar energy to eliminate environmental pollutants [1–7]. Among various semiconductors, some Aurivillius type bismuth-based oxide semiconductor materials such as BiOX (X = Cl, Br, I), BiVO$_4$ and Bi$_2$WO$_6$ have been widely used in photocatalysis [8–14].

Bismuth-based layered-structure compounds have a unique crystal structure and band structure. Hybridisation between 6s electrons of Bi and 2p electrons of O form chemical bonds which are stronger than those between Bi and other nonmetallic atoms (such as chalcogen), leading to a particularly stable (Bi-O)$^+$ layer. A series of Bi-based layered-structured photocatalytic materials of various band gap widths from 3.2 eV (e.g., BiOCl [15]) to 1.12–1.5 eV (e.g., Bi$_2$O$_2$S [16,17]) can be obtained by combining the (Bi-O)$^+$ layer with different anion layers. In addition, p-type (BiCuSO or the like) or n-type (Bi$_2$O$_2$CO$_3$, etc.) semiconductor materials can be obtained by adjusting the anion layer. Therefore, the different Bi-based oxide composite structure can not only control and broaden the range of light absorption of the catalyst, but also may form a hetero structure such as p-n junction.

Recently, Bi$_2$O$_2$CO$_3$, which is a member of the Aurivillius-type family and composed of [Bi$_2$O$_2$]$_{2+}$ layers interleaved by CO$_3$$^{2-}$ layers [18,19], has attracted growing concern because of its photocatalytic
ability to decompose organic pollutants in liquid phase and NO in gaseous phase [20–22]. Its unique layered structure, resulting in a large internal electrostatic field and asymmetric polarization effect, contributes to the separation of photogenerated electron-hole pairs [23,24]. However, the application of Bi$_2$O$_2$CO$_3$ in photodegradation is strongly limited by its large band gap (~3.3 eV). To overcome this limitation, many methods have been developed, such as the fabrication of heterojunctions such as BiVO$_4$/Bi$_2$O$_2$CO$_3$, Bi$_2$S$_3$/Bi$_2$O$_3$/Bi$_2$O$_2$CO$_3$ [25–27], noble metal deposition [28], elemental doping [29], and morphological modulation [30].

In this paper, we have synthesized S-doped Bi$_2$O$_2$(CO$_3$)$_{1−x}$S$_x$ by chemical bath precipitation, using Bi$_2$O$_2$CO$_3$ as the precursor, through the controlling of the precipitation process to have an intense effect over the photocatalytic properties. A nearly saturated S ratio and the best photocatalytic performance were observed in specimens with the most S content. With a negligible influence of the morphology and crystal structure, the optical absorption of Bi$_2$O$_2$CO$_3$ was extended from the ultraviolet (UV) to the visible region. The photocatalytic degradation of Congo Red showed that Bi$_2$O$_2$(CO$_3$)$_{1−x}$S$_x$ exhibited enhanced photoactivity in comparison to the precursor powder.

2. Results and Discussion

2.1. Synthetic Bi$_2$O$_2$(CO$_3$)$_{1−x}$S$_x$

Figure 1 shows the XRD(X-ray diffraction) pattern of the Bi$_2$O$_2$CO$_3$ powder prepared by hydrothermal method, together with a reference pattern of tetragonal Bi$_2$O$_2$CO$_3$ (JCPDS: 41–1488). No second phase can be found, and the sharp peaks indicate well-developed crystallinity. The preparation process of Bi$_2$O$_2$CO$_3$ can be summarized in Equations (1)–(3). CO$_3^{2-}$ forms through a hydrolysis reaction between (NH$_2$)$_2$CO and H$_2$O. Bi$_2$O$_3$ is also strongly hydrolyzed with water to produce (Bi$_2$O$_2$)$_{2+}$. The produced (Bi$_2$O$_2$)$_{2+}$ and CO$_3^{2−}$ then react to generate Bi$_2$O$_2$CO$_3$.

\[
\begin{align*}
(NH_2)_2CO + 2H_2O &\rightarrow 2NH_3^+ + CO_3^{2−} \\
Bi_2O_3 + 2H_2O &\rightarrow (Bi_2O_2)^{2+} + 2OH^+ \\
(Bi_2O_2)^{2+} + CO_3^{2−} &\rightarrow Bi_2O_2CO_3
\end{align*}
\] (1) (2) (3)

Figure 1. XRD pattern of hydrothermal synthesised Bi$_2$O$_2$CO$_3$. 

---

---

---
In addition, the percentage of crystallinity and the BET (Brunauer–Emmett–Teller) specific surface area of the samples with a $S:Bi_2O_2CO_3$ ratio $n$ equals to 0, 0.01, 0.02, 0.05, 0.10 and 0.20 (marked as M0, M1, M2, M5, M10 and M20, respectively) are shown in Table 1. There are no significant changes in their percentage of crystallinity, while samples of M5 and M10 display larger specific surface areas than that of other samples, which could lead to the exposure of more active sites for the photocatalytic experiment. The scanning electron microscopy (SEM) photograph and the high resolution transmission electron microscopy (HRTEM) images of the powder are shown in Figures 2 and 3. The morphology of the particles are nano-sized flakes of about 60–80 nm in thickness. In addition, the crystallinity of different samples calculated from the XRD results shows that $S$ doping introduced defects in the $Bi_2O_2CO_3$ and thus caused crystallinity change.

**Table 1.** Surface area and percentage of crystallinity of the $Bi_2O_2CO_3$ and M1–M20 powders.

|            | M0   | M1   | M2   | M5   | M10  | M20  |
|------------|------|------|------|------|------|------|
| Surface area (m$^2$/g) | 0.917 | 0.973 | 0.980 | 1.666 | 1.823 | 0.966 |
| Percentage of crystallinity (%) | – | 74.43 ± 0.96 | 65.62 ± 0.61 | 74.14 ± 0.88 | 77.31 ± 0.75 | 79.87 ± 1.75 |

![SEM photograph of hydrothermal synthesised $Bi_2O_2CO_3$.](image1)

**Figure 2.** SEM photograph of hydrothermal synthesised $Bi_2O_2CO_3$.

![HRTEM images of M0 (a); (b) and M20 (c); (d).](image2)

**Figure 3.** HRTEM images of M0 (a); (b) and M20 (c); (d).
The XRD patterns of the samples prepared by the Na$_2$S chemical bath precipitation are shown in Figure 4a. All diffraction peaks are consistent with Bi$_2$O$_2$CO$_3$, indicating that chemical bath precipitation did not introduce a significant second phase. The intensity of the diffraction peak does not obviously decrease, and the products still have good crystallinity. The position of the (013) diffraction peak for different samples are shown in Figure 4b. No obvious influence of Na$_2$S chemical precipitation on the crystal structure of Bi$_2$O$_2$CO$_3$ can be found because the position of the peak (013) did not show an apparent shift according to XRD results.

X-ray photoelectron spectroscopy (XPS) was utilized to obtain insights into the valence states and surface chemical compositions details of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$. As shown in Figure 5a, the XPS spectrum of Bi-4f shows two peaks at 159.05 and 164.35 eV, which belong to Bi-4f$_{7/2}$ and Bi-4f$_{5/2}$ energy levels, respectively. These two peaks are characteristic features of trivalent Bi in Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ [31]. The two peaks at 284.7 eV and 288.8 eV in Figure 5b show that the existence form of C is CO$_3^{2−}$ [32]. In Figure 5c, the two peaks are at 530.5 eV and 531 eV, which belong to O energy levels in B-O and CO$_3^{2−}$, respectively [33]. In Figure 5d, the peak of S-2p is at the range of 158−166 eV, which shows that the existence form of S is S$^{2−}$ [17]. On the other hand, the Bi-4f peak of M20 apparently shifts compared to M0 (Figure 5a), which proves that S takes place of CO$_3^{2−}$ partially [34].

![Figure 4](image-url)

**Figure 4.** (a) XRD patterns of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ prepared by chemical bath precipitation; (b) the position of the (013) diffraction.

![Figure 5](image-url)

**Figure 5.** XPS spectra of M0, M1, M2, M5, M10 and M20, Bi-4f (a); C−1s (b); O−1s (c); and S-2p (d).
Although Na$_2$S chemical precipitation had no obvious influence on the crystal structure of Bi$_2$O$_2$CO$_3$, the powder color was changed from white to yellow, and the color became darker as S: Bi$_2$O$_2$CO$_3$ molar ratio $n$ increased. The UV-Vis diffuse reflectance spectra are shown in Figure 6. Bi$_2$O$_2$CO$_3$ has a strong absorption of UV light with wavelengths less than 360 nm and weak absorption to 400 nm~500 nm-wavelength-visible light due to defects and oxygen vacancy, which also explained the fact that Bi$_2$O$_2$CO$_3$ could display visible light photocatalytic activity with the bandgap of 3.2 eV. With the introduction of S, the light absorption behaviour was significantly changed from M1 to M20. In particular, the absorption of visible light increased by about one order of magnitude. The band gap of Bi$_2$O$_2$CO$_3$ without sulfur is fitted as 3.27 eV, and the introduction of S leads to the emergence of a narrow band gap by lowering the conduction band position and meanwhile generating impurity levels [35,36]. The adsorption edge is around 380 nm. With the increase of S content, defects and oxygen vacancies increase, possibly due to point defects, and the fitted narrow band gap decreases from 3.25 to 2.20 eV. Energy levels of the valence band maximum (E$_{VB}$) were measured by the ultraviolet photoelectron spectrometer at UV intensity 500 nW and energy levels of the conduction band minimum (E$_{CB}$) were calculated by the bandgap. As shown in Figure 7, valence band edge position and conduction band edge position become more negative after the incorporation of sulfur into Bi$_2$O$_2$CO$_3$.

![Figure 6](image_url)

**Figure 6.** (a) UV-Vis diffuse reflectance spectra of the synthesized Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$; (b) band gap fitting with K-M relation.

The SEM observation showed that chemical bath treatment had little influence on the morphology of the Bi$_2$O$_2$CO$_3$ particles. EDS (energy dispersive spectroscopy) elemental mapping in Figure 8 revealed the homogeneous distribution of S on the particle surface, and no obvious segregation and
aggregation can be seen among the particles. The quantitative elemental analysis results are shown in Table 2. The S content in samples M1~M20 increases with the increase of $S$: Bi$_2$O$_2$CO$_3$ molar ratio $n$, but the S atom percentage (referring to Bi-content) is obviously smaller than $n$ and becomes stable as $n$ is greater than 0.10. This is consistent with the calculations about the surface adsorption of Bi$_2$O$_2$CO$_3$ by Chang [34], who suggested that $S^{2-}$ can be adsorbed in the oxygen vacancy of the (001) plane via the chemical bonding and reduce the surface energy. The calculation of the density of states near the Fermi level shows that the doping of $S$ can introduce a new energy level in the energy band and reduce the band gap. The electron state density near the Fermi surface is more diffusive, which favours the migration of electrons and therefore improves the photocatalytic performance.

![Figure 7](image.png)

**Figure 7.** Energy levels of the conduction band minimum ($E_{\text{CB}}$, red) and the valence band maximum ($E_{\text{VB}}$, black) calculated at theoretical pH = 0 (V is voltage; NHE is normalhydrogen electrode potential).

![Figure 8](image.png)

**Figure 8.** EDS element mapping details of M20 particles.
2.2. Ultraviolet-Visible Light Photocatalytic Properties of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$

The photocatalytic activity of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ was characterised by photocatalytic degradation of Congo Red. As is shown in Figure 9, the introduction of S could improve the photocatalytic activity of Bi$_2$O$_2$CO$_3$ under visible light and UV light. We measured the dye adsorption before switching on the light and normalized the concentrations, which made initial values of $c/c_0$ equal to 1 for all samples. The operation temperature used was around 0 °C. With pure Bi$_2$O$_2$CO$_3$, the Congo Red degrades by 41.6% under the irradiation of visible light for 3h, and by 46.1% under that of UV light, respectively. With the increase of molar ratio of S: Bi$_2$O$_2$CO$_3$ from 0.01 to 0.1, the degradation rate increases to 64.2% and 70.1%, respectively. The further increase of $n$, however, cannot further remarkably increase the degradation rate. At the highest molar ratio of S(0.2), the photocatalytic activity of Congo Red was 65.3% and 71.4%, respectively, which was 1.57 and 1.55 times higher than that of Bi$_2$O$_2$CO$_3$, respectively. The photo-degradation behavior of CR by use of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ obeys pseudo-first-order kinetics. This can be fitted by the Langmuir–Hinseluwood model of ln($c_0/c$) = $kt + A$, where $k$ is the reaction rate constant, $t$ is the degradation time and the intercept $A$ is the initial value of ln($c_0/c$), which means the dark adsorption of substrates. The $k$ value of M1, M2, M5, M10 and M20 under UV light is 4.3 × 10$^{-3}$ min$^{-1}$, 5.5 × 10$^{-3}$ min$^{-1}$, 6.1 × 10$^{-3}$ min$^{-1}$, 6.8 × 10$^{-3}$ min$^{-1}$ and 6.9 × 10$^{-3}$ min$^{-1}$, respectively. The $k$ value under visible light is 3.0 × 10$^{-3}$ min$^{-1}$, 3.5 × 10$^{-3}$ min$^{-1}$, 4.7 × 10$^{-3}$ min$^{-1}$, 5.5 × 10$^{-3}$ min$^{-1}$ and 5.9 × 10$^{-3}$ min$^{-1}$, respectively. The strong visible light sensitivity indicates higher utilization efficiency of solar light, making Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ a superior photocatalyst than the commercial P25 TiO$_2$, which has been reported to be hardly able to respond to visible light [37,38].

Chang’s theoretical calculations [34] suggest that S can be easily captured and adsorbed by oxygen vacancies on the surface of Bi$_2$O$_2$CO$_3$ as formed S$^{2-}$ can partially substitute CO$_3^{2-}$ without forming a second phase, introducing a bend built-in electric field. At the same time, their experiments also confirmed that Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ had higher conductivity and better carrier transport performance. The photoluminescence (PL) spectra of different S-substituted Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ (Figure 10) show that samples M10 and M20 displayed weaker electron holes and recombination, indicating that the introduction of S can effectively suppress the carrier recombination. The stronger light absorption contributed by the smaller band gap means more photo-induced electron hole generation, and those electron holes showed better separation according to PL spectra. It is worth noting that M20 has a stronger light absorption and smaller bandgap than that of M10, but that they present nearly the same photocatalytic activity, which may be caused by the smaller specific surface area (Table 1) and slightly weaker separation (Figure 10) of M20. Thus, all the three factors helped enhance the photocatalytic performance of Bi$_2$O$_2$CO$_3$ in our samples under UV and visible light irradiation.
ingure, the precipitate was separated and washed with deionized water and then dried at 70 °C. As-treated powders were numbered as M1, M2, M5, M10 and M20, respectively.

The hydrothermal tank was then tightly closed and kept in an oven at 180 °C for 50 mL of deionized water with the help of ultrasonic stirring for 10 min. After 8 h of further magnetic stirring at room temperature, the precipitates were filtered, washed with deionized water and ethanol and dried at 70 °C. As-treated powders were numbered as M1, M2, M5, M10 and M20, respectively.

Figure 9. Degradation of Congo Red under the irradiation of (a,c) UV, and (b,d) visible light, with \( \text{Bi}_2\text{O}_2(\text{CO}_3)_{1-x}\text{S}_x \); (e) the degradation rate as a function of \( n = (\text{S}: \text{Bi}_2\text{O}_2\text{CO}_3) \).

Figure 10. Photoluminescence spectra of \( \text{Bi}_2\text{O}_2(\text{CO}_3)_{1-x}\text{S}_x \).
3. Materials and Methods

3.1. Preparation of the Precursor Powder Bi₂O₂CO₃ via Hydrothermal Method

Three grams of urea (≥99.0%, Beijing Modern Orient Fine Chemistry Co. Ltd., Beijing, China) was dissolved in 60 mL of deionized water in a Teflon hydrothermal tank. 4.65 g Bi₂O₃ powder (99.99%, Aladdin Industrial Corporation, Shanghai, China) was then introduced into the solution. The hydrothermal tank was then tightly closed and kept in an oven at 180 °C for 12 h. After cooling down to room temperature, the precipitate was separated and washed with deionized water and ethanol several times and then dried in the oven at 70°C.

3.2. Preparation of Bi₂O₂(CO₃)₁₋ₓSₓ by Chemical Bath Precipitation

Five suspensions of Bi₂O₂CO₃ were prepared, each by dispersing 2.04 g of Bi₂O₂CO₃ powder in 50 mL of deionized water with the help of ultrasonic stirring for 10 min. A certain amount (S:Bi₂O₂CO₃ ratio n, equals to 0.01, 0.02, 0.05, 0.10 and 0.20, respectively) of 0.5 mol/L Na₂S (≥98.0%, Shanghai Tongya Chemical Technology Co. Ltd., Shanghai, China) solution was introduced into the respective suspensions. After 8 h of further magnetic stirring at room temperature, the precipitates were separated and washed several times with deionized water and ethanol and dried at 70°C. As-treated powders were numbered as M1, M2, M5, M10 and M20, respectively.

3.3. Characterization

Powder X-ray diffraction (XRD) was completed on a diffractometer (D8-Advance, Bruker, Billerica, MA, USA) using monochromatized Cu Kα (λ = 0.15418 nm) radiation with scanning speed of 3°/min. The morphology of the samples were carried out on a scanning electron microscope (JSM-7001F, JEOL, Tokyo, Japan) operating at a 5 kV and a field emission electron microscope (JEM-2100F, JEOL). The surface areas of specimens were tested on an automated gas sorption analyzer (Quantachrome, autosorb iQ2). The X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi instrument. A UV-Vis-NIR spectrometer (Lambda 950, PerkinElmer, Waltham, MA, USA) was used to measure UV-Vis diffuse reflectance spectra (DRS). Energy levels of the valence band maximum (EᵥB) were measured by the ultraviolet photoelectron spectrometer (AC-2, RIKEN KEIKI, Tokyo, Japan).

3.4. Photocatalytic Test

The photocatalytic activity of the prepared Bi₂O₂(CO₃)₁₋ₓSₓ powder samples was evaluated by photodegrading Congo Red (CR, 100 mg/L) aqueous solution. The reason we chose this concentration is because it is proper to evaluate the change of the color. 0.16 g photocatalyst powder specimen was dispersed into 80 mL CR solution and stirred in the dark for 2 h to reach adsorption–desorption equilibrium between the photocatalysts and organic dye molecules. Magnetic stirring and a cooling-water bath were held continuously to prevent thermal effect during the degradation process and to keep the uniformity. A 5W LED with emission wavelength of 365 ± 5 nm and a 300 W xenon lamp with 420 nm cut-off filters were used as the UV (365~800 nm) and visible light sources (420~800 nm), respectively. The incident light source was placed above the aqueous solution vertically, and the illumination intensity for UV and visible lights at upper surface of the solution were about 78 mW/cm² and 132 mW/cm². The photocatalytic processes were conducted under constant temperature, using ice water to cool the system. At the end of regular time intervals, 3 mL suspension was collected and centrifuged, and the residual CR concentration in the supernatant fluid was analyzed by UV-vis spectrophotometer (UV–3100, Hitachi, Tokyo, Japan).
4. Conclusions

AnNa$_2$S chemical bath treatment of Bi$_2$O$_2$CO$_3$ did not generate a second phase. It is shown that the introduction of S can effectively broaden the optical absorption range, although it does not apparently change the crystal structure of Bi$_2$O$_2$CO$_3$. The electrons at the top of the valence band in Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ can be excited by shorter wavelengths of sunlight, forming photo-generated electron-hole pairs. This may be due to the formation of chemical bonds between the S$^2-$ and vacancies on the surface of Bi$_2$O$_2$CO$_3$ crystal, which can affect the surface properties.

Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ can improve the catalytic performance of visible and UV regions to a certain extent by the introduction of S in Bi$_2$O$_2$CO$_3$ by chemical bath. This is because the introduction of S can effectively suppress the carrier recombination and improve the carrier transport performance. However, S can be introduced only into the surface of Bi$_2$O$_2$CO$_3$ by chemical bath at room temperature, and the improvement of catalytic performance is limited.

Author Contributions: Y.L. and J.D. designed the project; J.D. conducted the most experiments; L.Q. and H.X. performed party of the experiments; J.D. and H.W. together wrote and revised the manuscript with input from all the authors. C.N. and Y.L. took part in discussing and the revision of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tong, H.; Ouyang, S.; Bi, Y.; Umezawa, N.; Oshikiri, M.; Ye, J. Nano-photocatalytic materials: Possibilities and challenges. Adv. Mater. 2012, 24, 229–251. [CrossRef] [PubMed]
2. Wang, P.; Huang, B.B.; Dai, Y.; Whangbo, M.H. Plasmonic photocatalysts: Harvesting visible light with noble metal nanoparticles. Phys. Chem. Chem. Phys. 2012, 14, 9813–9825. [CrossRef] [PubMed]
3. Wang, H.L.; Zhang, L.S.; Chen, Z.G.; Hu, J.Q.; Li, S.J.; Wang, Z.H.; Liu, J.S.; Wang, X.C. Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. Chem. Soc. Rev. 2014, 43, 5234–5244. [CrossRef] [PubMed]
4. Moniz, S.J.A.; Shevlin, S.A.; Martin, D.J.; Guo, Z.X.; Tang, J.W. Visible-light driven heterojunction photocatalysts for water splitting—A critical review. Energy Environ. Sci. 2015, 8, 731–759. [CrossRef]
5. Yu, J.G.; Low, J.X.; Xiao, W.; Zhou, P.; Jaroniec, M. Enhanced photocatalytic CO$_2$-reduction activity of anatase TiO$_2$ by coexposed \{001\} and \{101\} facets. J. Am. Chem. Soc. 2014, 136, 8839–8842. [CrossRef] [PubMed]
6. Chava, R.K.; Do, J.Y.; Kang, M. Hydrothermal growth of two dimensional hierarchical MoS$_2$ nanospheres on one dimensional Cds nanorods for high performance and stable visible photocatalytic H$_2$ evolution. Appl. Surf. Sci. 2018, 433, 240–248. [CrossRef]
7. Chava, R.K.; Do, J.Y.; Kang, M. Fabrication of Cds-Ag$_3$PO$_4$ heteronanostructures for improved visible photocatalytic hydrogen evolution. J. Alloys Compd. 2017, 727, 86–93. [CrossRef]
8. Ye, L.Q.; Su, Y.R.; Jin, X.L.; Xie, H.Q.; Zhang, C. Recent advances in BiOX (X = Cl, Br and I) photocatalysts: Synthesis, modification, facet effects and mechanisms. Environ. Sci. Nano 2014, 1, 90–112. [CrossRef]
9. Xiao, X.; Liu, C.; Hu, R.; Zuo, X.; Nan, J.; Li, L.; Wang, L. Oxygen-rich bismuth oxyhalides: Generalized one-pot synthesis, band structures and visible light photocatalytic properties. J. Mater. Chem. 2012, 22, 22840–22843. [CrossRef]
10. Kim, T.W.; Choi, K.S. Nanoporous BiVO$_4$ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. Science 2014, 343, 990–994. [CrossRef] [PubMed]
11. Kudo, A.; Omori, K.; Kato, H. A novel aqueous process for preparation of crystal form-controlled and highly crystalline BiVO$_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. J. Am. Chem. Soc. 2000, 31, 11459–11467. [CrossRef]
12. Zhou, L.; Jin, C.G.; Yu, Y.; Chi, F.L.; Ran, S.L.; Lv, Y.H. Molten salt synthesis of Bi$_2$WO$_6$ powders with enhanced visible-light induced photocatalytic activities. J. Alloys Compd. 2016, 680, 301–308. [CrossRef]
13. Zhang, J.; Huang, L.H.; Yang, L.X.; Lu, Z.D.; Wang, X.Y.; Xu, G.L.; Zhang, E.P.; Wang, H.B.; Kong, Z.; Xi, J.H.; et al. Controllable synthesis of Bi2WO6 (001)/TiO2 (001) heterostructure with enhanced photocatalytic activity. J. Alloys Compd. 2016, 676, 37–45. [CrossRef]

14. Kalithasan, N.; Hari, C.B.; Rajesh, J.T. Photocatalytic efficiency of bismuth oxyhalide (Br, Cl and I) nanoparticles for RhB dye degradation under LED irradiation. J. Ind. Eng. Chem. 2016, 34, 146–156.

15. Zhang, H.; Yang, Y.; Zhou, Z.; Zhao, Y.; Liu, L. Enhanced photocatalytic properties in BiOBr nanosheets with dominantly exposed (102) facets. J. Phys. Chem. C 2014, 118, 14662–14669. [CrossRef]

16. Zhang, X.; Liu, Y.; Zhang, G.; Wang, Y.; Zhang, H.; Huang, F. Thermal decomposition of bismuth oxysulfide from photoelectric Bi2O3S to Superconducting Bi4O5S3. ACS Appl. Mater. Interfaces 2015, 7, 4442–4448. [CrossRef] [PubMed]

17. Pacquette, A.L.; Hagiwara, H.; Ishihara, T.; Gewirth, A.A. Fabrication of an oxysulfide of bismuth BiO3S to Superconducting Bi4O5S3 microspheres. Solid State Sci. 2016, 27, 27–36. [CrossRef]

18. Tsunoda, Y.; Sugimoto, W.; Sugahara, Y. Intercalation behavior of n-alkylamines into a protonated from of a layered perovskite derived from aurivilius phase Bi2SrTa2O6. Chem. Mater. 2003, 15, 632–635. [CrossRef]

19. Huang, Y.; Wang, W.; Zhang, Q.; Cao, J.J.; Huang, R.J.; Ho, W.K.; Lee, S.C. In Situ fabrication of a-Bi2O3/(Bi2O3)3 nanosheet hetrojunctions with tunable optical property and photocatalytic activity. Sci. Rep. 2016, 6, 23455. [CrossRef] [PubMed]

20. Ni, Z.L.; Sun, Y.J.; Zhang, Y.X.; Dong, F. Fabrication, modification and application of (BiO)2CO3-based photocatalysts: A review. Appl. Surf. Sci. 2016, 365, 314–335. [CrossRef]

21. Cheng, H.F.; Huang, B.B.; Yang, K.S.; Wang, Z.Y.; Qin, X.Y.; Zhang, X.Y.; Dai, Y. Facile template-free synthesis of Bi2O3CO3 hierarchical microflowers and their associated photocatalytic activity. J. Phys. Chem. C 2010, 11, 2167–2173. [CrossRef] [PubMed]

22. Dong, F.; Xiong, T.; Sun, Y.J.; Huang, H.W.; Wu, Z.B. Synergistic integration of thermocatalysis and photocatalysis on black defective (Bi2O3)3 microspheres. J. Mater. Chem. A 2015, 3, 18466–18474. [CrossRef]

23. Huang, H.W.; Wang, J.J.; Dong, F.; Guo, Y.X.; Tian, N.; Zhang, Y.H.; Zhang, T.R. Highly Efficient Bi2O3CO3 Single-Crystal Lamellas with Dominantly Exposed {001} Facets. Cryst. Growth Des. 2015, 15, 534–537. [CrossRef]

24. Huang, H.W.; Tian, N.; Jin, S.F.; Zhang, Y.H.; Wang, S.B. Syntheses, characterization and nonlinear optical properties of a bismuth subcarbonate Bi2O3CO3. Solid State Sci. 2014, 30, 1–5. [CrossRef]

25. Madhusudan, P.; Ran, J.R.; Zhang, J.; Yu, J.G.; Liu, G. Novel urea assisted hydrothermal synthesis of hierarchical BiO3/ Bi2O3CO3 nanocomposites with enhanced visible-light photocatalytic activity. Appl. Catal. B 2011, 110, 286–295. [CrossRef]

26. Liang, N.; Zai, J.T.; Xu, M.; Zhu, Q.; Wei, X.; Qian, X.F. Novel Bi2O3/Bi2O3CO3 heterojunction photocatalysts with enhanced visible light responsive activity and wastewater treatment. J. Mater. Chem. A 2014, 2, 4208–4216. [CrossRef]

27. Huang, Y.; Fan, W.; Long, B.; Li, H.; Zhao, F.; Liu, Z.; Tong, Y.; Ji, H. Visible light Bi2O3/Bi2O3/Bi2O3CO3 photocatalyst for effective degradation of organic pollutants. Appl. Catal. B Environ. 2016, 185, 68–76. [CrossRef]

28. Dong, F.; Li, Q.Y.; Sun, Y.J.; Ho, W.K. Noble metal-like behavior of plasmonic Bi particles as a cocatalyst deposited on (Bi2O3)3 microspheres for efficient visible light photocatalysis. ACS Catal. 2014, 4, 4341–4350. [CrossRef]

29. Xiong, T.; Huang, H.W.; Sun, Y.J.; Dong, F. In-Situ synthesis of a C-doped (Bi2O3)3 hierarchical self-assembly effectively promoting visible light photocatalysis. J. Mater. Chem. A 2015, 3, 6118–6127. [CrossRef]

30. Huang, H.W.; Xiao, K.; Yu, S.X.; Dong, F.; Zhang, T.R.; Zhang, Y.H. Iodide surface decoration: An facile and efficacious approach to modulating the band energy level of semiconductors for high performance visible-light Photocatalysis. Chem. Commun. 2016, 52, 354–357. [CrossRef] [PubMed]

31. Dong, F.; Li, Q.; Ho, W.; Wu, Z.B. The mechanism of enhanced visible light photocatalysis with micro-structurally optimized and graphene oxide coupled (Bi2O3)3. Clin. Sci. Bull. 2015, 60, 1915–1923.

32. Li, Q.; Liu, H.; Dong, F.; Fu, M. Hydrothermal formation of N-doped (Bi2O3)3 honeycomb-like microspheres photocatalysts with bismuth citrate and Dicyandiamide as precursors. J. Colloid Interface Sci. 2013, 408, 33–42. [CrossRef] [PubMed]

33. Liu, Y.; Wang, Z.; Huang, B.; Yang, K.; Zhang, X.; Qin, X.; Dai, Y. Preparation, electronic structure, and photocatalytic properties of Bi2O2CO3 nanosheet. Appl. Surf. Sci. 2010, 257, 172–175. [CrossRef]
34. Chang, C.; Teng, F.; Liu, Z. Fully Understanding the Photochemical Properties of Bi$_2$O$_2$(CO$_3$)$_{1-x}$S$_x$ Nanosheets. *Langmuir* **2016**, *32*, 3811–3819. [CrossRef] [PubMed]

35. Huang, H.; Li, X.; Wang, J.; Dong, F.; Chu, P.K.; Zhang, T.; Zhang, Y. Anionic Group Self-Doping as a Promising Strategy: Band-Gap Engineering and Multi-Functional Applications of High-Performance CO$_2^2$–Doped Bi$_2$O$_2$CO$_3$. *ACS Catal.* **2015**, *5*, 4094–4103. [CrossRef]

36. Zhao, Z.; Zhou, Y.; Wang, F.; Zhang, K.; Yu, S.; Cao, K. Polyaniline-Decorated (001) Facets of Bi$_2$O$_2$CO$_3$Nanosheets: In Situ Oxygen Vacancy Formation and Enhanced Visible Light Photocatalytic Activity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 730–737. [CrossRef] [PubMed]

37. Pawar, R.C.; Khare, V.; Lee, C.S. Hybrid photocatalysts using graphitic carbon nitride/cadmium sulfide/reduced graphene oxide (g-C$_3$N$_4$/CdS/RGO) for superior photodegradation of organic pollutants under UV and visible light. *Dalton Trans.* **2014**, *43*, 12514–12527. [CrossRef] [PubMed]

38. Liu, G.; Chen, Z.; Dong, C.; Zhao, Y.; Li, F.; Lu, G.Q.; Cheng, H.-M. Visible Light Photocatalyst: Iodine-Doped Mesoporous Titania with a Bicrystalline Framework. *J. Phys. Chem. B* **2006**, *110*, 20823–20828. [CrossRef] [PubMed]