Direct Z-Scheme Cs$_2$O–Bi$_2$O$_3$–ZnO Heterostructures as Efficient Sunlight-Driven Photocatalysts

Abdo Hezam,† K. Namratha,† Deepalekshmi Ponnamma,‡ Q. A. Drmosh,§ Adel Morshed Nagi Saeed,‖ Chun Cheng,*,⊥ and K. Byrappa*†‡§

†Center for Materials Science and Technology, University of Mysore, Vijana Bhavana, Manasagangothiri, Mysuru 570 006, India
‡Center for Advanced Materials, Qatar University, P.O. Box 2713, Doha, Qatar
§Physics Department and Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
‖Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, JSS Science & Technology University, Mysuru 570 006, India
*Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, P. R. China

Supporting Information

ABSTRACT: Limited light absorption, inefficient electron–hole separation, and unsuitable positions of conduction band bottom and/or valence band top are three major critical issues associated with high-efficiency photocatalytic water treatment. An attempt has been carried out here to address these issues through the synthesis of direct Z-scheme Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructures via a facile, fast, and economic method: solution combustions synthesis. The photocatalytic performances are examined by the 4-chlorophenol degradation test under simulated sunlight irradiation. UV–vis diffuse reflectance spectroscopy analysis, electrochemical impedance test, and the observed transient photocurrent responses prove not only the significance of Cs$_2$O in extending light absorption to visible and near-infrared regions but also its involvement in charge carrier separation. Radical-trapping experiments verify the direct Z-scheme approach followed by the charge carriers in heterostructured Cs$_2$O–Bi$_2$O$_3$–ZnO photocatalysts. The Z-scheme carrier carrier pathway induced by the presence of Cs$_2$O has emerged as the reason behind the efficient charge carrier separation and high photocatalytic activity.

INTRODUCTION

One of the major technical concerns of today is the treatment and conservation of water. The great significance of this area lies in its human need both in environmental and life aspects. Population and industrial explosion all over the world severely affected water bodies to a great extent and is now creating many ecological imbalances. Recent years have witnessed development of numerous materials to solve environmental issues and to conserve water and energy.¹–³ As far as water bodies are concerned, different types of organic pollutants are daily discharged into them, equally affecting the aquatic and nonaquatic living beings. In order to keep the environment sustainable, researchers are trying to remove these toxic organic pollutants using solar energy.⁴ Although photocatalytic water treatment has been a topic of investigation for several years, it remains in the laboratory level because of various economic and technical issues.⁵

Generally, when the photocatalysis process occurs on a typical semiconductor surface, two simultaneous reactions of oxidation and reduction take place because of the photo-induced positive holes and the negative electrons. Though numerous metal oxides such as TiO$_2$, Fe$_2$O$_3$, ZnO, WO$_3$, ZrO$_2$, and so forth gained large popularity in photocatalysis, they have been associated with several issues leading to decreased efficiency and performance.⁶ At first, some of these metal oxides (TiO$_2$ and ZnO) have large band gaps, preventing the absorption of visible light. Rapid electron–hole (e/h) recombination and improper positions of conduction band bottom (CBB) and valence band top (VBT) in some metal oxides are other two issues associated with them. In order to overcome these issues, many practices of modification/doping of metal oxide materials are being practiced.⁷–¹²

Metal-oxide heterostructures attract remarkable current research attention as they can extend the visible light absorption (if one of the coupled semiconductors has a small band gap), suppress the e/h recombination rate, and provide a platform to engineer the positions of CBB and VBT.⁷,¹³,¹⁴ Normally, two main mechanisms are used to explain the charge carrier migration pathway (i) formation of junctions at the interfaces among the coupled metal oxides (heterojunction)
and (ii) formation of Z-scheme systems (see the Supporting Information Scheme S1). The suitable mechanism is selected based on the energy structure of the coupled semiconductors and the detected reactive species during the photocatalysis process.

Efficiency of charge separation enhances upon the formation of typical junctions between the coupled semiconductors. However, in the heterojunction, the electrons transport to the semiconductor with a more positive CBB, and the holes migrate to the semiconductor with a more negative VBT, finally leading to decrease the redox ability, and thus, negatively affects the photocatalytic activity of the heterojunction. In contrast to this, the Z-scheme heterostructure allows the migration of electrons to the semiconductor with a more negative CBB and accumulation of the holes at the semiconductor with a more positive VBT. This will provide a platform for a higher photocatalytic activity.

However, the Z-scheme heterostructure requires electron mediators, mostly in the liquid form in the first generation Z-scheme and noble metal in the second generation. The liquid electron mediator limits the applications of the first generation and the noble metal electron mediator increases the cost of photocatalysts.

Very recently, the third generation of the Z-scheme came to the scenario as the most desired one for the photocatalytic degradation of pollutants because it does not require electron mediators. To synthesize an efficient direct Z-scheme photocatalyst, its components have to be selected carefully. The band gap, work function, VBT, and CBB of the components should be calculated prior to the synthesis. Another significant condition to be satisfied is that at least one of the components should have a small band gap to extend the absorption to the visible range. The CBB and VBT have to be matched as well. The CBB potential of at least one of the components should be negative enough over $E_0$ ($^{\text{CS}}$O$_2^\text{-}/$O$_2$) (−0.046 eV vs normal hydrogen electrode), and the VBT of at least one of the components should be more positive than the standard redox potential of $^{\text{OH}}$/OH$^−$ (+1.99 eV). Obeying all these criteria, several direct Z-scheme systems including g-$\text{C}_3\text{N}_4$, ZnO, g-$\text{C}_3\text{N}_4$/MnO$_2$, AgI/Bi$_2$Sn$_2$O$_7$, graphene quantum dots/ZnO nanowires, Fe$_2$O$_3$/Cu$_2$O, and Cu$_2$ZnSn$_2$O$_6$ were synthesized and applied successfully in photocatalytic applications.

The Bi$_2$O$_3$–ZnO heterostructure reported efficient photocatalysis toward degrading organic pollutants under UV and visible light. In addition to this, ternary combinations based on Bi$_2$O$_3$–ZnO heterostructures such as Ag–Bi$_2$O$_3$–ZnO and Bi$_2$O$_3$–CeO$_2$–ZnO were also well established as efficient sunlight/visible light-driven photocatalysts in photocatalytic water treatment. However, the charge migration pathway in all these reported Bi$_2$O$_3$–ZnO-based heterostructures follows the heterojunction approach which negatively affects the redox potential and thereby the photocatalytic activity. This substantiates the need of sputtering the semiconducting heterostructures to harvest maximum efficiency of photocatalysis from them.

Herein, we prepare a novel Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure using a simple solution combustion synthesis (SCS) and explore its photocatalytic activity. SCS is considered as a sustainable and green alternative to the widely used time- and/or energy-consuming synthesis routes. By this specific preparation, large-scale production of photocatalysts in low cost is targeted to satisfy industrial requirements. The significance of this ternary metal-oxide heterostructure is well-addressed by comparing with the binary systems and pristine Cs$_2$O under the same conditions. The photocatalytic activities of all heterostructures are examined by degradation of the 4-chlorophenol (4-CP) model pollutant. The enhanced photocatalytic activity of Cs$_2$O–Bi$_2$O$_3$–ZnO is explored by means of radical trapping power tools. Moreover, the mechanism of the direct Z-scheme heterostructure is demonstrated clearly by substantiating its applicability to all electromagnetic irradiations.

## RESULTS AND DISCUSSION

### Crystal Structure and Morphology

X-ray diffraction (XRD) patterns of Cs$_2$O–Bi$_2$O$_3$–ZnO (sample CBZ15) and Bi$_2$O$_3$–ZnO heterostructures (sample CBZ0) are compared in Figure 1a. The characteristics peaks of Cs$_2$O appear on the spectrum of CBZ15 at $2\theta$ = 18.2°, 25.7°, and 42.51° (JCPDS 09-0104). The peaks at 31.69°, 34.83°, and 36.16° for both CBZ15 and CBZ0 samples correspond to the hexagonal phases of ZnO (JCPDS 36-1451). The remaining peaks observed are attributed to SCS during which gases were released. Scanning electron microscopy (SEM) micrographs in Figure 1b,c show that the Cs$_2$O–Bi$_2$O$_3$–ZnO exhibits a 3D sponge-like structure with numerous irregular pores. The porous network is mainly attributed to SCS during which gases were released. This porous structure is able to increase the efficiency of charge separation enhances upon the formation of typical junctions between the coupled semiconductors. However, in the heterojunction, the electrons transport to the semiconductor with a more positive CBB, and the holes migrate to the semiconductor with a more negative VBT, finally leading to decrease the redox ability, and thus, negatively affects the photocatalytic activity of the heterojunction.

Figure 1. (a) XRD patterns of the samples CBZ0 (Bi$_2$O$_3$–ZnO) and CBZ15 (Cs$_2$O–Bi$_2$O$_3$–ZnO), (b) and (c) SEM, (d) TEM, and (e) HRTEM images of the sample CBZ15.
pollutant nanoparticle contact and accordingly enhances the photocatalytic efficiency. However, the SEM images do not accurately provide the size and morphology of individual nanoparticles, and this is rectified by the transmission electron microscopy (TEM) image of Figure 1d. The size of Bi$_2$O$_3$–Cs$_2$O–ZnO nanoparticles is calculated using imaging processing software ImageJ with the scale bar obtained during TEM achievement as a reference to be <10 nm.

The lattice fringe values of CBZ15 are further explored from the high-resolution TEM (HRTEM) image (Figure 1e). The observed values of about 0.52, 0.32, and 0.34 nm, respectively, correspond to the (002) plane of ZnO (JCPDS card no. 36-1451),57 (121) plane of Bi$_2$O$_3$ (JCPDS card No. 71-0465),48 and the (012) plane of Cs$_2$O (JCPDS card no. 09-0104).49 This result confirms the formation of the Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure and is in good agreement with the XRD observations.

**X-ray Photoelectron Spectroscopy Analysis.** Formation of the Z-scheme Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure is well explained by means of XPS analysis as given in Figure 2. All characteristic peaks of Bi, Zn, Cs, and O are seen in the spectra, without any additional impurities other than the C 1s peak coming from the carbon tape in the XPS sample holder (Figure 2a). There are three O 1s peaks located at 530.4 (O I), 532.1 (O II), and 533.8 eV (O III) (Figure 2b). While the O I is associated with the lattice O$_2$, the O II and O III are, respectively, due to OH and adsorbed H$_2$O.33,50,51

In order to get a deep insight into the charge carrier migration pathway, high-resolution XPS of Zn 2p, Cs 3d, and Bi 4f was carried out (Figure 2c–e). Both Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ are located, respectively, at 1023.3 and 1046.4 eV (Figure 2c), which exhibit upward shifts compared to the standard positions of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ for pure ZnO.52 However, the binding energy difference between Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ for the Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure is observed to be 23.1 eV, which is almost the same for pure ZnO, implying a normal state of Zn$^{2+}$ in the Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure.52

For pure Bi$_2$O$_3$, the Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ peaks are observed respectively at 163.9 and 158.6 eV,40 whereas, in the present case, these peaks (Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$) are found to be upward-shifted to 164.9 and 159.6 eV, respectively (Figure 2e). The reported XPS peaks of Cs 3d at 725.2 eV for Cs 3d$_{5/2}$ at 739.2 eV for Cs 3d$_{3/2}$ in other samples, are addressed using the reported XPS peaks of Cs 3d at 725.2 eV for Cs 3d$_{5/2}$ and 739.2 eV for Cs 3d$_{3/2}$, which are observed to be downward-shifted to respective positions of 724.4 and 738.5 eV in the Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure (Figure 2d). In short, the upward shifts observed in the positions of Zn 2p$_{3/2}$, Zn 2p$_{1/2}$, Bi 4f$_{5/2}$, and Bi 4f$_{7/2}$ and the downward shifts observed in the positions of Cs 3d$_{5/2}$ and Cs 3d$_{3/2}$ confirm that the electrons migrate from the Bi$_2$O$_3$ CB and ZnO CB to Cs$_2$O CB (Scheme S1).53 These observed peak shifts also indicate a possibility of a strong interaction between Cs$_2$O, Bi$_2$O$_3$, and ZnO.

**Photocatalytic Studies.** Photocatalytic activities of synthesized Cs$_2$O–Bi$_2$O$_3$–ZnO are addressed using the colorless model organic contaminant 4-CP. This organic compound is a toxic, poor biodegradable contaminant even at low concentrations and widely observed in industrial wastewater treatment.55,56 Moreover 4-CP is chosen as a colorless pollutant to assure the absence of the sensitization effect and hence to accurately evaluate the photocatalytic activity of the prepared heterostructures. Figure 3a shows the time-dependent adsorption (in the dark) and degradation of 4-CP by different samples under simulated solar irradiation. A slight decrease in the concentration of 4-CP is noted during the first 40 min of stirring in the dark because of the adsorption of 4-CP on the surface of photocatalysts. However, the concentration of 4-CP remains unchanged thereafter.

As illustrated in Figure 3a, coupling Bi$_2$O$_3$–ZnO with Cs$_2$O greatly enhances the photodegradation efficiency. The photodegradation percentages of 4-CP are, respectively, 50.9, 21.1, 45, 48.1, 40.2, 79.3, 95.6, 98.5, and 87% for the samples TiO$_2$–P25, Cs$_2$O, Cs$_2$O–ZnO, Cs$_2$O–Bi$_2$O$_3$, CBZ0, CBZ5, CBZ10, CBZ15, and CBZ20 after 80 min exposure in simulated solar irradiation. Importantly, it is observed that degradation efficiency increases with increasing the concentration of Cs$_2$O, and the highest photocatalytic degradation is obtained at 15 mol % Cs$_2$O. Beyond 15 mol % Cs$_2$O, degradation performance remarkably decreases, indicating that the 15 mol % Cs$_2$O is the optimal concentration. Figure 3b shows the degradation kinetics of 4-CP over Cs$_2$O–Bi$_2$O$_3$–ZnO which...
follows a pseudo-first-order reaction. The k constants of different samples calculated from the slopes of $-\ln(C/C_0)$ plots are 0.019, 0.038, 0.053, 0.0238, 0.008, 0.0072, 0.0067, 0.0052, and 0.0026 min$^{-1}$ for CBZ5, CBZ15, CBZ20, TiO$_2$–P25, Cs$_2$O–Bi$_2$O$_3$, Cs$_2$O–ZnO, CBZ0, and Cs$_2$O, respectively. Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructures (CBZ5, CBZ10, CBZ15, and CBZ20) show higher sunlight photocatalytic performance when compared to the standard photocatalyst TiO$_2$–P25, whereas the binary heterostructures (Cs$_2$O–Bi$_2$O$_3$, Cs$_2$O–ZnO, and Bi$_2$O$_3$–ZnO) exhibit lower photocatalytic activity. Finally, the degradation efficiency monitored is following the trend CBZ15 > CBZ10 > CBZ20 > CBZ5 > TiO$_2$–P25 > Cs$_2$O–Bi$_2$O$_3$ > Cs$_2$O–ZnO > CBZ0 > Cs$_2$O (i.e., the degradation efficiency of Cs$_2$O–Bi$_2$O$_3$–ZnO > TiO$_2$–P25 > Cs$_2$O–Bi$_2$O$_3$ > Cs$_2$O–ZnO > Bi$_2$O$_3$–ZnO > Cs$_2$O).

Effect of Catalyst Dosage. The catalyst dosage is an important parameter to explore the pollutant degradation mechanism.$^{57-59}$ To study the effect of catalyst dosage on degradation efficiency, the degradation reaction was repeated using different concentrations of the sample CBZ 15 under identical conditions, and the results obtained are displayed in Figure 3c. It can be seen that photocatalytic efficiency increases with increasing the catalyst concentration from 0.1 to 0.4 g/L. Beyond 0.4 g/L of catalysts, the photocatalytic degradation of 4-CP decreased, implying this specific concentration as the optimal catalyst dosage.

The increase in 4-CP degradation with respect to catalysts is due to increasing the number of photocatalytic active sites, whereas the decrease in photocatalytic degradation after the optimal catalyst dosage is due to the light scattering by the catalyst particles that affect light absorption and thus the number of produced reactive species.

Effect of Initial Concentration. The effect of initial 4-CP concentration on the photodegradation ability of the Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure was examined by varying the concentration from 10 to 50 mg L$^{-1}$ under 80 min of simulated solar irradiation. As shown in Figure 3d, the photocatalytic degradation efficiency decreased with increasing the initial concentration of 4-CP. Higher 4-CP concentration causes more molecules to be present around the photocatalytic active sites and thus inhibits light penetration to the catalyst surface and reduces the e/h$^+$ pair generation. As a result, the generation of $O_2^-$ and $OH$ is reduced and hence the photocatalytic performance.$^{60}$

Reusability and Mineralization Degree. The photostability of the heterostructured Cs$_2$O–Bi$_2$O$_3$–ZnO photocatalyst is investigated by reusing it (sample CBZ15) for five sequential cycles. As displayed in Figure S1a, a negligible decrease in 4-CP degradation performance is observed even after five consecutive cycles, confirming the superior photostability of Cs$_2$O–Bi$_2$O$_3$–ZnO.

To further validate the photostability of Cs$_2$O–Bi$_2$O$_3$–ZnO, the XRD pattern of the optimized Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructure (sample CBZ15) is recorded before the photocatalysis experiment and after five cycles of photodegradation. Figure S1b shows that there is no remarkable change in the XRD pattern after the fifth cycle of photodegradation. The observed photostability is benefited from the direct Z-scheme charge carrier migration pathway,$^{23}$ that is, the photogenerated electrons in ZnO and Bi$_2$O$_3$ are consumed by recombination with the photogenerated holes in the VB of Cs$_2$O.

The total organic carbon (TOC) test is an essential index for exploring the mineralization degree of an organic pollutant.$^{61}$ To clarify whether 4-CP was mineralized or degraded by the heterostructured Cs$_2$O–Bi$_2$O$_3$–ZnO, TOC analysis was adopted. The degradation and mineralization of 4-CP under simulated solar irradiation as a function of time were compared and are presented in Figure S1c. Apparently, about 82% of 4-CP was mineralized in 80 min, indicating the powerful photocatalytic activity of the heterostructure synthesized.

UV–Vis Diffuse Reflectance Spectroscopy Studies. To investigate the enhanced photocatalytic activity of Cs$_2$O–Bi$_2$O$_3$–ZnO, UV–vis diffuse reflectance spectroscopy (DRS) was recorded for various samples. As shown in Figure 4a, the coupling between Cs$_2$O and Bi$_2$O$_3$–ZnO heterostructures resulted in significant enhancement in light absorption in the
visible and near-infrared (NIR) regions. The highest light absorption is exhibited by Cs$_2$O−Bi$_2$O$_3$−ZnO with 15 mol % Cs$_2$O (sample CBZ15), and this is the major reason for its highest photocatalytic degradation efficiency. In other words, the enhancement in light absorption increases the number of photogenerated electrons and holes, increases the number of active species (*OH and *$O_2^-$), and thereby improves the photocatalytic activity.

**Electrochemical Studies.** The photocurrent response is an important criterion to assess e/h separation and the photocatalytic activity. The role of Cs$_2$O was further investigated by monitoring the photocurrent responses of the Bi$_2$O$_3$−ZnO heterostructure (sample CBZ0) and Cs$_2$O−Bi$_2$O$_3$−ZnO heterostructures (samples CBZ5, CBZ10, CBZ15, and CBZ 20). The results obtained are represented in Figure 4b. The photocurrent density of Cs$_2$O−Bi$_2$O$_3$−ZnO samples increases to a maximum value and then slowly declines and achieves a steady state. Apparently, the Bi$_2$O$_3$−ZnO heterostructure (sample CBZ0) shows low photocurrent density, indicating the quick e/h recombination in it, whereas Cs$_2$O−Bi$_2$O$_3$−ZnO heterostructures (samples CBZ5, CBZ10, CBZ15, and CBZ20) show notable enhancement in photocurrent responses. This is attributed to the enhancement of separation efficiency of photogenerated e/h through the electronic interaction among Cs$_2$O, Bi$_2$O$_3$, and ZnO. The highest photocurrent intensity and highest 4-CP degradation efficiency obtained for the sample CBZ15 confirm the significant role of charge separation in enhancing the photocatalytic activity.

For further validating the efficiency of photogenerated e/h separation, electrochemical impedance values were checked for all fabricated heterostructures (Figure 4c). Compared to other samples, CBZ0 displays the largest arc radius in the electrochemical impedance Nyquist plot, demonstrating its high interfacial charge transfer resistance and low charge separation efficiency. The samples CBZ5, CBZ10, CBZ15, and CBZ20 exhibit a significant decrease in the arc radius of the Nyquist plot, confirming the low interfacial resistance and high charge-carrier separation efficiency. Obviously, the sample CBZ15 shows the smallest arc radius and thereby achieves the highest charge-carrier separation efficiency. Electrochemical impedance values thus well agree with the results of photocurrent responses. Thus, the electrochemical studies reveal the impact of Cs$_2$O on the reactivity properties of Cs$_2$O−Bi$_2$O$_3$−ZnO heterostructures.

**Band Position Determination and Charge Carrier Migration Pathway.** Estimating the CBB and VBT is vital to the evaluation of a photocatalyst for pollutant degradation. Figure 5a shows UV−vis DRS spectra of pristine Cs$_2$O, Bi$_2$O$_3$, and ZnO. Cs$_2$O shows the highest visible light absorption followed by Bi$_2$O$_3$. The band gaps ($E_g$) are calculated from Tauc’s plot to be 1.92 eV for Cs$_2$O (direct band gap), 3.1 eV for ZnO (direct band gap), and 2.76 eV for Bi$_2$O$_3$ (indirect band gap). The CBB and VBT are calculated using the following equations and presented in Table S1.

\[
\begin{align*}
\text{VBT} & = \chi - E_{H^+} + 0.5E_g \\
\text{CBB} & = E_g - \text{VBT}
\end{align*}
\]

where $\chi$ is electronegativity and $E_{H^+}$ represents the energy of free electrons on the hydrogen scale. Furthermore, the VBT was estimated using valence band XPS analysis as shown in the supporting information Figure S2 to be 0.42, 2.88, and 2.82 eV for Cs$_2$O, Bi$_2$O$_3$, and ZnO, respectively. The CBB was calculated and is presented in Table S2. The CBB was found to be −1.5, 0.12, and −0.28 eV for Cs$_2$O, Bi$_2$O$_3$, and ZnO, respectively.

On the basis of these results, the position of the Cs$_2$O CBB (−1.5 eV) is more negative compared to the Bi$_2$O$_3$ CBB (0.12 eV) and ZnO CBB (−0.28 eV). Thus, electrons are supposed to move from the Cs$_2$O CB to Bi$_2$O$_3$ CB and ZnO CB if Cs$_2$O−Bi$_2$O$_3$−ZnO is a heterojunction system (see Scheme 1). However, the high-resolution XPS analysis indicates that the electrons migrate from the Bi$_2$O$_3$ CB and ZnO CB to Cs$_2$O CB. Hence, Cs$_2$O−Bi$_2$O$_3$−ZnO is not a heterojunction system.

In fact, the electron migration pathway is better explained by the Z-scheme approach as depicted in Scheme 1; that is, under irradiation with the appropriate wavelength of light, the electrons are promoted from the VB of each semiconductor (Bi$_2$O$_3$, ZnO, and Cs$_2$O) to its VB, leaving holes behind. Then, the electrons migrate from the CB of ZnO to the CB of Bi$_2$O$_3$ because the CBB potential of Bi$_2$O$_3$ (0.12 eV) is more positive than that of ZnO (−0.28 eV). Meanwhile, the electrons of the ZnO CB and Bi$_2$O$_3$ CB combine with holes in the Cs$_2$O VB. The electrons do not stop at the Cs$_2$O VB, but they are photoexcited to the Cs$_2$O CB. This process continues under appropriate irradiation, leading to high enhancement in the charge separation.

**Mechanism of Pollutant Degradation.** To understand the charge migration pathway and the photocatalytic degradation mechanism of 4-CP, trapping experiments were performed to identify the main radicals responsible for the degradation process. To trap the free radicals, tert-butyl alcohol (TBA) was used as an *OH scavenger and benzoquinone (BQ) as an *O$_2^-$ scavenger. In addition, KI and AgNO$_3$ were used as holes and electrons scavengers, respectively.

The photocatalytic degradation of 4-CP over the sample CBZ15 was repeated under identical conditions in the presence of BQ and TBA separately. As displayed in Figure 6a, a remarkable inhibition of 4-CP photodegradation in the presence of BQ suggests the prominent role of *O$_2^-$ reactive...
species in 4-CP photocatalytic degradation. In addition to this, the drastic decrease in degradation of 4-CP in the presence of TBA indicates the significant role played by $\cdot$OH radicals also in the photodegradation of 4-CP over the Cs$_2$O–Bi$_2$O$_3$–ZnO photocatalyst. In contrast, the addition of KI (hole scavengers) led to significant enhancement in the degradation efficiency of Cs$_2$O–Bi$_2$O$_3$–ZnO; 99.2% of 4-CP was degraded in 60 min only, and this is attributed to improvement in the charge separation efficiency, that is, the absence of holes reducing the recombination rate of e/h, and thereby increases the concentration of electrons which react with O$_2$ to produce $\cdot$O$_2^-$. However, no significant effect on photodegradation was observed in the presence of AgNO$_3$, indicating that the electrons do not play a direct role in the photodegradation process.

The formation of $\cdot$OH-free radicals was further confirmed by liquid photoluminescence (PL) detection through the reaction of $\cdot$OH with terephthalic acid (TA).

To further endorse the formation of $\cdot$O$_2^-$, spin-trapping electron spin resonance (ESR) was used to detect $\cdot$O$_2^-$ formation by employing a 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) free radical trapping agent in methanol. The ESR signals of CBZ15 under simulated solar light irradiation and in the dark were recorded and are represented in Figure 6c. No peaks were observed in the dark, whereas the characteristic peaks of DMPO–$\cdot$O$_2^-$ appear under simulated sunlight irradiation with increased intensity with irradiation time. This indicates the formation of $\cdot$O$_2^-$ under simulated sunlight irradiation.

On the basis of all these results, a typical pollutant degradation mechanism is designed for Cs$_2$O–Bi$_2$O$_3$–ZnO heterostructures as shown in Figure 6d. The charge transport in heterostructured photocatalysts is generally explained by one of the two mechanisms—heterojunction mechanism or Z-scheme mechanism. Evidence obtained from XPS results reveals the nonapplicability of the heterojunction mechanism in explaining the charge carrier migration pathways in Bi$_2$O$_3$–ZnO–Cs$_2$O. If the heterojunction mechanism is followed, the electrons are supposed to be accumulated in the CB of Bi$_2$O$_3$ which has the lowest CBB among the three metal oxides. However, the potential of the...
CBB of Bi2O3 is not sufficient to produce \(^{1}O_2\) radicals confirmed from the spin-trapping ESR experiments, thereby discarding the possibility of the heterojunction mechanism. In contrast, the Z-scheme mechanism can explain the charge transporting processes in Bi2O3-ZnO-Cs2O heterostructures very well. Under simulated sunlight irradiation, all Bi2O3, ZnO, and Cs2O absorb light energy according to UV-vis DRS spectra and generate e/h pairs. The electrons will then migrate from the CB of Bi2O3 and the CB of ZnO and combine with holes in the VB of Cs2O. Hence, the e/h pairs are efficiently separated. The CBB potential of Cs2O (−1.5 eV) is more negative than the redox potential of O2/\(^{1}O_2\) (−0.046 eV).26

Thus, the electrons accumulated in the CB of Cs2O exhibit strong reducibility and easily reduce O2 into \(^{1}O_2\)−. At the same time, the holes retained in the VB of ZnO show enough oxidability to oxidize H2O into \(*OH\) radicals because the VB potential of ZnO is more positive than the redox potential of \(*OH/\text{OH}^-\) or \(*OH/H_2O\) (+1.99 eV).27 The Z-scheme mechanism thus clearly evidences photodegradation of 4-CP, supported by the scavengers, PL, and spin-trapping ESR results. Therefore, all the results strongly indicate that the Cs2O−Bi2O3−ZnO heterostructure follows the direct Z-scheme mechanism rather than the heterojunction mechanism.

■ CONCLUSIONS

Novel Cs2O−Bi2O3−ZnO heterostructures consisting of nanoparticles of <10 nm size were synthesized by means of the solution combustion method. The concentration of Cs2O was varied to derive the maximum photactivity of the heterostructure, and an optimal ratio is observed at 15 mol % Cs2O. The fabricated Cs2O−Bi2O3−ZnO heterostructure showed a superior photocatalytic activity and photostability by degrading the model organic pollutant 4-CP. High-resolution XPS analysis and radical scavengers/trapping experiments were used to confirm the direct Z-scheme charge migration mechanism in the heterostructure. The direct Z-scheme charge migration pathway not only enhances the charge separation efficiency but also causes the accumulation of photogenerated electrons and holes in the corresponding energy bands (CB/VB) with the highest redox potential. The novel Cs2O−Bi2O3−ZnO structures fabricated were able to absorb UV, visible, and NIR wavelengths, confirming their applicability toward any radiation. It is also anticipated that these kinds of heterostructures can be used not only for photocatalytic degradation but also for different applications including H2 and O2 production, reduction of CO2, and sensing.

■ EXPERIMENTAL SECTION

Materials. CsNO3 (Alfa Aesar, 99.9%), Zn(NO3)2·6H2O (Alfa Aesar, 99%), Bi(NO3)3·5H2O (Sigma-Aldrich, 98%), glycine (Sigma-Aldrich, 99%), and 4-CP (Alfa Aesar, 99%) were of analytical grade and used as received. Deionized water (18.2 MΩ cm) was used in the experiments.

Synthesis Method. An appropriate amount of Bi(NO3)3·5H2O was dissolved in 1.2 M HNO3 to form 30 ml of 1.18 M Bi(NO3)3·5H2O in a separate beaker (BS), and 30 ml of 0.82 M Zn(NO3)2·6H2O was prepared separately in a beaker (ZS). Equal volumes of BS and ZS were mixed in five separate beakers. A different quantity of CsNO3 was added to each beaker in a way to obtain 0, 5, 10, 15, and 20 mol % Cs2O, and the corresponding samples were labeled as CBZ0, CBZ5, CBZ10, CBZ15, and CBZ20, respectively. (oxidizer). The appropriate amount of glycine as a fuel was added to each beaker in such a way that the fuel/oxidizer valence ratio of the mixture equals one. Each solution was stirred for 30 min and heated on a hot plate at 320 °C. After dehydration, the solution started to boil, foam, and then ignite. The obtained powder was light orange. Cs2O, Bi2O3, ZnO, Cs2O−Bi2O3, and Cs2O−ZnO were prepared using the same procedure.

Characterizations. The crystal patterns were recorded using a powder X-ray diffractometer (XRD, Rigaku smart Lab-II, Cu Kα radiation, λ = 1.5414 Å). The morphology of the prepared samples was investigated using SEM (Hitachi-3400N) and HRTEM (Jeol/JEM 2100). XPS spectra of the samples were obtained using an ESCALAB 250Xi, Thermo Scientific instrument. DRS UV−vis spectra were recorded using a Thermo scientific Evolution 201 UV−visible spectrophotometer. A JES FA200 spectrometer was used to examine the ESR signals of spin-trapped radicals.

Photocatalytic Test. The photocatalytic activities of the prepared heterostructures were examined toward the degradation of 4-CP as a colorless pollutant model under simulated sunlight irradiation. A 300 W Xenon lamp was used as the light source. Typically, 0.04 g of the prepared catalyst was dispersed in a separate reactor containing 100 mL 4-CP (10 mg/L). The suspension was stirred in the dark for 1 h to accomplish the desorption−adsorption equilibrium before being illuminated. About 3 mL of the suspension was sampled at every 20 min and subjected to centrifugation to remove the photocatalyst. A Beckman Coulter DU 730 UV−vis spectrophotometer was used to measure the concentration of 4-CP, whereas its mineralization degree was measured on a TOC analyzer (Shimadzu TOC-V CPN).

Electrochemical Studies. Photocurrent measurements for the fabricated heterostructures were carried out using a CHI 608e electrochemical analyzer. Fluorine-doped tin oxide glasses spin-coated with the prepared heterostructures were used as working electrodes. A platinum wire and a Ag/AgCl electrode were used as counter and reference electrodes, and 0.5 M Na2SO4 was used as the electrolyte during the photocurrent measurements. The working electrode was irradiated at 100 mW cm−2 obtained from a 300 W xenon lamp, and the photocurrent was measured at 0 V during light on-off cycling. Electrochemical impedance spectroscopy was carried out using the same setup at an open circuit potential with an ac voltage magnitude of 5 mV over the frequency range of 10⁶ to 1 Hz.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01449.

Photostability, TOC, DRS UV−vis spectra, photocurrent response, and electrochemical impedance measurements of the prepared samples (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

E-mail: kbyrappa@gmail.com. Phone: +91-821-2419422.
E-mail: chengc@sustc.edu.cn. Phone: +86 0755-88018568.
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