Visible-Light-Driven CO_2 Reduction into Methanol Utilizing Sol-Gel-Prepared CeO_2-Coupled Bi_2O_3 Nanocomposite Heterojunctions

Mohamed Mokhtar Mohamed Mostafa [1,*], Ahmed Shawky [2,*], Sharif Fakhruz Zaman [3],
Katabathini Narasimharao [1], Mohamed Abdel Salam [1], Abdulmohsen Ali Alshehri [1], Nezar H. Khdary [4],
Sulaiman Al-Faifi [1] and Abhishek Dutta Chowdhury [5]

[1] Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203,
    Jeddah 21589, Saudi Arabia
[2] Nanomaterials and Nanotechnology Department, Advanced Materials Institute, Central Metallurgical R&D
    Institute (CMRDI), P.O. Box 87, Cairo 11421, Egypt
[3] Chemical and Materials Engineering Department, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[4] King Abdulaziz City for Science and Technology, Riyadh 11442, Saudi Arabia
[5] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
*   Correspondence: mmoustafa@kau.edu.sa (M.M.M.M.); phyashawky@gmail.com (A.S.)

Abstract: Carbon dioxide (CO_2) photoreduction into renewable fuels over semiconductor photocatalysts has emerged as a green and sustainable alternative for energy production. Consequently, tremendous efforts are being performed to develop robust and sustainable photocatalysts. Therefore, visible-light active nanocomposite photocatalysts composed of 5.0–20.0 wt.% bismuth oxide (Bi_2O_3) and cerium oxide (CeO_2) were synthesized by a sol-gel-based process. The prepared nanocomposites were evaluated for the promoted photocatalytic reduction of CO_2 into methanol (CH_3OH). Various characterizations of the obtained photocatalysts exposed an outstanding development of crystalline structure, morphology, and surface texture due to the presence of Bi_2O_3. Moreover, the absorbance of light in the visible regime was improved with enhanced charge separation, as revealed by the exploration of optical response, photoluminescence, and photocurrent measurements. The overall bandgap calculations revealed a reduction to 2.75 eV for 15% Bi_2O_3/CeO_2 compared to 2.93 eV for pure CeO_2. Moreover, the adjusted 2.8 g L^{-1} dose of 15% Bi_2O_3/CeO_2 selectively produced 1300 μmol g^{-1} CH_3OH after 9 h of visible light irradiation. This photocatalyst also exhibits bearable reusability five times. The improved progression of 15% Bi_2O_3/CeO_2 is denoted by significant charge separation as well as enhanced mobility. This study suggests the application of metal oxide-based heterojunctions for renewable fuel production under visible light.

Keywords: heterojunction photocatalysts; nanostructures; CO_2 conversion; fuel generation; visible light activity

1. Introduction

With the development of the industrial revolution in the last two centuries, several industries have evolved, such as cement [1], fertilizers [2], and aerosols [3]. In addition, the rapid growth of the population with not enough environmental awareness has led to the release of massive waste materials through several activities [4]. The release of greenhouse gases proportionally increased and contributed to the significant rise in the earth's temperature, with a threat value close to 1.5 °C [5,6]. Thus, reducing, capturing, or recycling greenhouse gases is a matter of life or death for humanity. Carbon dioxide gas (CO_2) is the primary source of global warming that is currently humped due to various human activities ranging from burning fossil fuels to the rapid development of several industries [7,8]. There are several approaches for reducing CO_2 emissions through the use of

renewable energy sources or recycling the released CO_2 into value-added products [9–13]. The photoconversion of CO_2 into valuable and renewable hydrocarbon fuels on semiconductor photocatalysts has caused substantial apprehension toward the clean invention of alternative energy resources [14–17]. The photoreduction of CO_2 either in the gas or liquid phase is an ecological pathway owing to its simplicity and sustainability, particularly regarding conservational topics [18,19]. The catalytic conversion of CO_2 into value-added products, such as methanol (CH_3OH) or other organic materials, is an additional benefit to the global warming issue [17,20,21]. As a consequence, plentiful research is currently being performed to advance this approach by utilizing simulated and natural solar light [22–24]. In the meantime, abundant ceramic-based photocatalysts demonstrate effectual progress in several fields, such as pollutant degradation and fuel production [25–29]. Notably, TiO_2 and ZnO represent famous oxides for fuel production and the photocatalytic reduction of CO_2 owing to their suitable reduction potential balanced within their bandgap energies (E_g) [30–33]. However, the extended E_g, photostability in solutions, and the rapid recombination of the photoinduced charges are key issues in the realization of these oxides [34,35]. Therefore, there are several efforts regarding the coupling of these oxides with more stable ceramics to enhance their stability [31,36–38]. The use of other stable ceramic oxides with comparable E_g represents an alternative path [39,40].

Interestingly, the use of rare-earth metal oxides such as cerium oxide (CeO_2) is promising in photocatalysis. In a recent study by Hezam et al., the nanostructured CeO_2 with controlled oxygen vacancies could be efficient for the photoreduction of CO_2 into CH_3OH [41]. Moreover, CeO_2 has narrower E_g (2.8~3.1 eV) than TiO_2 and ZnO, exhibiting an n-type character and representing a more stable ceramic oxide with potential applications in various photocatalytic reactions, including water splitting [42], organic transformation reactions [43], and pollutant degradation [44]. Moreover, the coupling with p-type oxides such as bismuth oxides (Bi_2O_3) showed a significant photocatalytic performance in dye degradation [37,45], self-cleaning coatings [46], and NO oxidation [47]. In a recent study performed by Yang et al., the β-Bi_2O_3-loaded CeO_2 heterostructure photocatalyst exhibited a significant redox for the oxidation of stable antibiotic molecules due to the enhanced charge separation of the added β-Bi_2O_3 in the heterojunction system [48]. Moreover, Masula et al. investigated the improved photocatalytic performance of Bi_2O_3/CeO_2 nanocomposites for the mineralization of wastewater pollutants in a short time due to their enhanced visible-light absorbance [49]. However, there are no studies regarding the photoreduction of CO_2 as far as we know. It could be of great scientific and industrial benefit regarding the ability of this nanocomposite in the renewable reforming of CO_2 into valuable and usable fuels. In this regard, nanostructured CeO_2 was simply prepared using the polymeric surfactant-assisted sol-gel method and subsequently coupled with 5.0~20.0 wt.% of Bi_2O_3. The prepared Bi_2O_3/CeO_2 heterojunctions featured a mesoporous surface texture, amended light harvesting, and superior photogenerated charge separations as concluded from the detailed characterization. The photoreduction of CO_2 into selective CH_3OH production over the optimized 15% Bi_2O_3/CeO_2 presented a generation rate of 144.4 μmol g^{-1} h^{-1} and demonstrated robust stability for regeneration.

2. Results and Discussion

2.1. Structural, Surface, and Optical Investigations of the Produced Photocatalysts

The formed materials were identified by XRD graphs as described in Figure 1 for the pure sample in **a** compared to the Bi^{3+}-added samples in **b**, **c**, **d**, and **e** for 5, 10, 15, and 20 wt.%. The pure sample **a** was identically identified as pure CeO_2 by the coincident 2θ values of 28.5°, 32.8°, 47.5°, 56.0°, and 59.1° to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of cubic CeO_2 as described in JCPDS card No. 34–0394, respectively [50]. Similarly, the 5% Bi^{3+} precursor addition (represented by **b**) did not alter the overall pattern due to the limited detection of minor contamination of the XRD instrument. However, the further addition of the Bi^{3+} precursor in **c**~**e** resulted in the appearance of new diffraction peaks, mainly existing at 27.6°, 35.2°, 39.1°, 45.1°, and 45.4° assigned to (201), (200), (321),

(222), and (421) of the β-phase of Bi_2O_3 (JCPDS No. 76–0147) [20]. Thus, the Bi_2O_3/CeO_2 nanocomposite formation was revealed by XRD depiction [51].
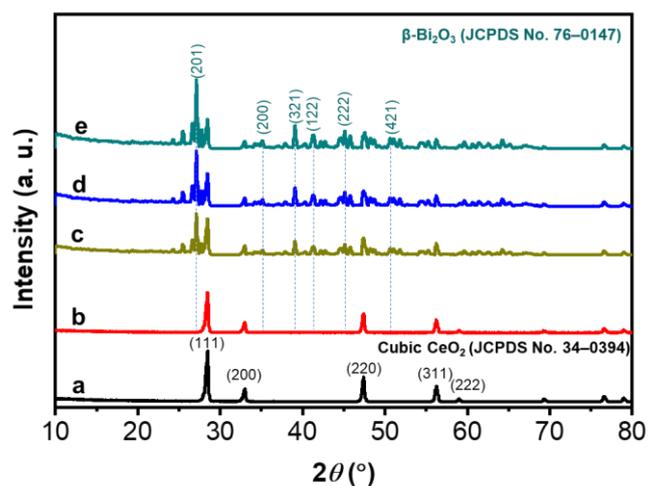

Figure 1. XRD patterns of the produced powders representing the crystallization of pure CeO_2 (as labeled in **a** compared with 5, 10, 15, and 20% Bi_2O_3/CeO_2 as represented by **b**, **c**, **d**, and **e**, respectively.

TEM images describing the morphology of the pure CeO_2 compared with various Bi_2O_3-added CeO_2 nanostructures can be seen in Figure 2. The pure CeO_2 indicated the formation of irregular-shaped nanocrystals with well-defined edges (Figure 2a). The particle size of the CeO_2 nanocrystals ranged between 20 and 40 nm. The magnified elected area at a high resolution (Figure 2b) confirmed the face-centered cubic phase of CeO_2 owing to the d-spacing measurement of 0.31 nm representing the (111) plane [46]. The Bi_2O_3-loading of CeO_2 revealed certain changes to the structure and morphology as seen in Figure 2c–h. In Figure 2c, representing 5% Bi_2O_3/CeO_2, small spherical nanoparticles were seen side-by-side with the CeO_2 nanocrystals of <10 nm as represented by black–white arrows [51]. The high-resolution TEM image of the selected part of this revealed the formation of Bi_2O_3 nanocrystals due to the measured d-spacing (0.2 nm) of the (222) plane as shown in Figure 2d [48]. On the other hand, the higher content of Bi_2O_3 at 10 wt.% (Figure 2e) and 15 wt.% (Figure 2g) showed an elongation of its Bi_2O_3 structure assigned by the representative black–white arrows. The Bi_2O_3 was grown in a rod-like morphology but maintained the same crystalline phase as confirmed by the d-spacing measurements in the high-resolution images (Figure 2f,h) without any effect on the CeO_2 nanocrystals. This refers to the fact that the solution-based β-Bi_2O_3 is usually grown in a rod-like structure [20,40,49]. These findings indicate the successful fabrication of the Bi_2O_3/CeO_2 heterojunction. The close contact between the Bi_2O_3 and CeO_2 could enhance the charge transfer amongst them and explain the efficient photocatalytic activity toward the production of CH_3OH [48,49,51].

To clarify the surface texture of the obtained Bi_2O_3/CeO_2 heterojunctions, the N_2 adsorption–desorption isotherms comparing pure CeO_2 and 15% Bi_2O_3/CeO_2 photocatalysts are shown in Figure 3. Both samples exhibited minor adsorption at a relative pressure (P/P_0) of 0.65 and an H2-hysteresis loop with type IV until P/P_0 = 0.94 [45]. This finding designates that the prepared samples parade a mesoporous structure. The inclusion of Bi_2O_3 has no significant effect on the superficial structure but slightly changes the S_{BET} and pore diameters (inset of Figure 3). The determined S_{BET} is comparatively decreased by including Bi_2O_3 to CeO_2 from 191 to 169 $m^2 g^{-1}$ (for 15% Bi_2O_3/CeO_2, Table 1) owing to the spread of smaller-sized Bi_2O_3 on the surface of CeO_2. However, the pore size is almost the same (8.92 nm for CeO_2 and 8.87 nm for 15% Bi_2O_3/CeO_2) as seen in the inset of Figure 3.
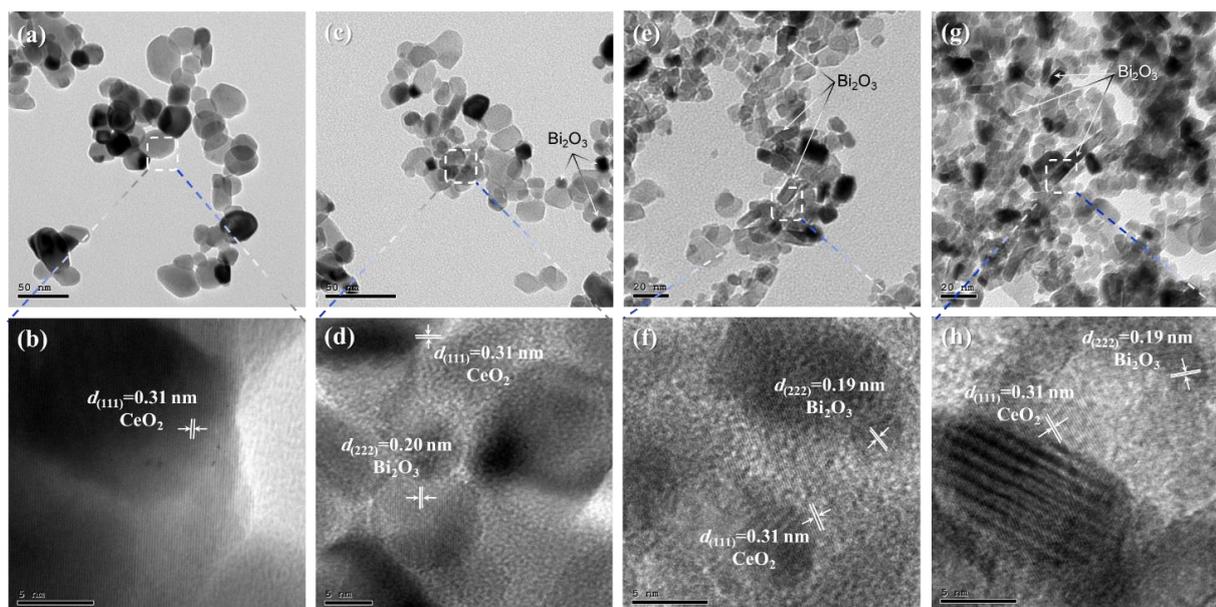
Figure 2. TEM investigations (up) and the corresponding high-resolution imaging for the selected area (down) of pure CeO_2 (**a,b**), 5% Bi_2O_3/CeO_2 (**c,d**), 10% Bi_2O_3/CeO_2 (**e,f**), and 15% Bi_2O_3/CeO_2 (**g,h**).
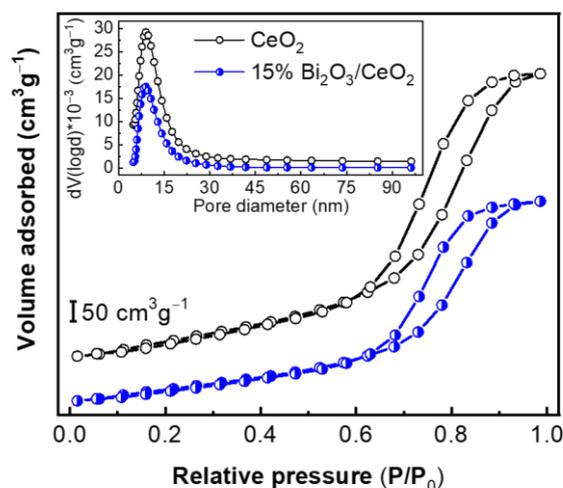

Figure 3. N_2 adsorption/desorption isotherms and corresponding pore size distribution (inset) for prepared CeO_2 compared to 15% Bi_2O_3/CeO_2 heterojunctions as indicated.

Table 1. Consequence of Bi_2O_3 inclusion on physicochemical characteristics of CeO_2, namely, surface area (S_{BET}), absorption edge (Abs. edge), and determined bandgap energies (E_g). The consistent photoreduction of CO_2 to CH_3OH after 9 h irradiation is listed. The corresponding photocurrent intensities are also stated in the last column.

Sample	S_{BET} $(m^2\ g^{-1})$	Abs. Edge (nm)	E_g (eV)	CH_3OH Generation $(\mu m\ g^{-1})$	Photocurrent $(\mu A\ cm^{-2})$
CeO_2	191	423	2.93	70 ($\pm$2.8)	11.56
5% Bi_2O_3/CeO_2	183	427	2.89	360 ($\pm$12.6)	28.92
10% Bi_2O_3/CeO_2	174	442	2.82	720 ($\pm$21.6)	43.52
15% Bi_2O_3/CeO_2	169	453	2.75	1080 ($\pm$24.5)	51.54
20% Bi_2O_3/CeO_2	163	454	2.74	1100 ($\pm$38.4)	51.81

The surface composition of the 15% Bi_2O_3/CeO_2 sample was analyzed via XPS as seen in Figure 4. The Bi 4f the high-resolution spectrum (Figure 4a) was deconvoluted into two

oxidation states for the majority of Bi^{3+} at binding energies of 164.2 and 159.2 eV for $4f_{5/2}$ and $4f_{7/2}$, respectively, and a minority of Bi^{5+} at 165.0 and 160.5 eV for the corresponding mentioned orbitals [49]. The Ce 3d spectrum (Figure 4b) was deconvoluted into the co-existing minority Ce^{3+} and the majority of Ce^{4+} [44]. The Ce^{3+} is located at 902.1 and 886.5 for $3d_{3/2}$ and $3d_{5/2}$ orbitals [46]. On the other hand, the major peaks located at 917.2, 908.2, and 898.7 eV are attributed to the $3d_{3/2}$ binding of Ce^{4+} while the binding energies positioned at 890.2 and 883.1 eV correspond to the $3d_{5/2}$ of Ce^{4+} in CeO_2. In Figure 4c, the O1s spectrum is deconvoluted into three peaks at 532.4, 530.1, and 529.0 eV assigned to the adsorbed oxygen species, the lattice bonding Bi–O of β-Bi_2O_3, and the lattice bonding Ce–O in CeO_2, respectively [47]. Thus, the confirmation of the formed Bi_2O_3/CeO_2 heterojunction is established by the XPS study. The quantitative analysis using the instrumental software showed the content of Bi_2O_3 in this sample at 13.9 wt.%.
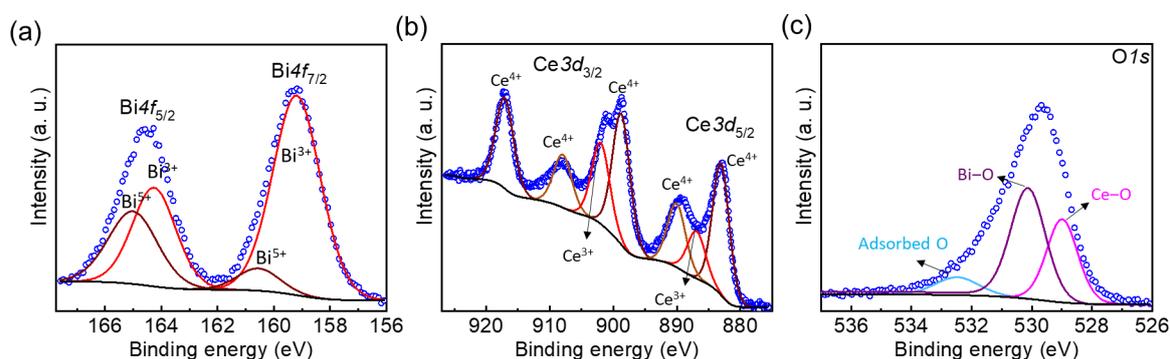

Figure 4. XPS analysis at high resolution for Bi 4f (**a**), Ce 3d (**b**), and O 1s (**c**) of the 15% Bi_2O_3/CeO_2 heterojunction.

The light harvesting by the synthesized photocatalysts was also investigated as displayed in Figure 5. The pristine CeO_2 disclosed a minor visible-light absorbance with an absorption edge at 423 nm and an estimated E_g of 2.93 eV [43]. However, the synthesized Bi_2O_3/CeO_2 showed an extension of the visible-light harvesting as the absorption edges shifted toward longer wavelengths due to the low-bandgap Bi_2O_3 [48]. The presence of 5, 10, 15, and 20 wt.% Bi_2O_3 in CeO_2 redshifted the absorption edges to 427, 442, 453, and 454 nm, with corresponding E_g values of 2.89, 2.82, 2.75, and 2.74 eV, respectively (Table 1, inset of Figure 5). Thus, the presence of Bi_2O_3 could enhance light harvesting and associated photocatalytic performance [37,49].
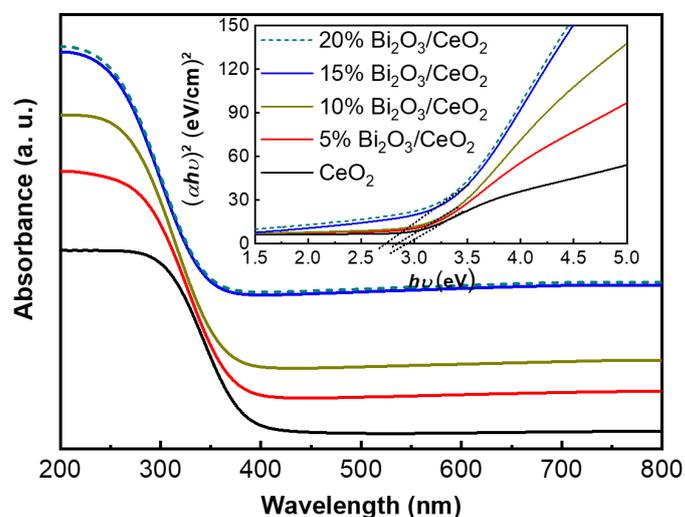

Figure 5. Light absorption spectra of the prepared CeO_2 compared with Bi_2O_3/CeO_2 heterojunctions and their corresponding calculated energy gaps as seen in the inset.

2.2. Photoreduction of CO_2 over Bi_2O_3/CeO_2 Heterojunctions

The photocatalytic progression of the produced Bi_2O_3/CeO_2 is evaluated for the reduction of CO_2 as described in Figure 6 compared to the pure CeO_2. In Figure 6a, the photocatalytic generation of CH_3OH of Bi_2O_3/CeO_2 is much higher than the pure CeO_2 after 9 h of light irradiation as seen in Table 1. The production rate of CH_3OH reached 120.0 and 122.2 µmol g^{-1} h^{-1} by 15 and 20% Bi_2O_3/CeO_2, respectively, which is almost 15.4 and 15.7 times higher than the pure CeO_2 at the same 2.0 gL^{-1} dose (7.8 µmol g^{-1} h^{-1}, Figure 6b). As a result, the photoreduction of CO_2 into CH_3OH can be surged by governing the amount of Bi_2O_3. The 15 wt.% of Bi_2O_3 is chosen as the optimal included amount in the Bi_2O_3/CeO_2 heterojunction based on the above results.
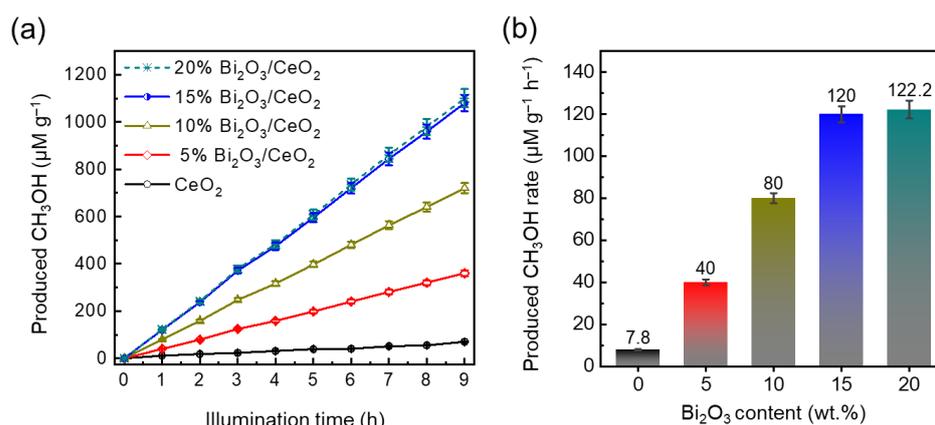

Figure 6. Photocatalytic production of CH_3OH utilizing the produced CeO_2 and Bi_2O_3/CeO_2 heterojunctions as in (**a**). The influence of adding Bi_2O_3 on the generation rate of produced CH_3OH is illustrated in (**b**).

Photoluminescence (PL) spectral emission and photocurrent intensity are regarded as powerful means for understanding the photocatalytic activity promotion of the 15% Bi_2O_3/CeO_2 as seen in Figure 7 [41,52,53]. In Figure 7a, we can see that the pure CeO_2 exhibited an intensive PL peak positioned at 406.3 nm due to the large recombination of the photogenerated charges [44]. The introduction of 5, 10, 15, and 20 wt.% Bi_2O_3 amounts clearly quenched the PL intensity by 12, 21, 32, and 32.1%, respectively. These results indicate the suppression of the charge carrier's recombination rates. So, the catalytic activity could be increased by the long-life charge carriers as proved in previous PL quenching due to the precise Bi_2O_3 occurrence in the 15% Bi_2O_3/CeO_2 heterojunction. Moreover, transient photocurrent measurements have also established the best photocatalytic performance of the same 15% Bi_2O_3/CeO_2 nanocomposite as presented in Figure 7b and Table 1. The 15% Bi_2O_3/CeO_2 exhibited the largest photocurrent value (51.54 µA cm^{-2}), which is almost 4.5 times higher than the photocurrent generated from pure CeO_2. This finding reveals the promoted charge mobility due to the superior separation of the photoinduced charge carriers. Accordingly, the photoreduction rate of CO_2 could be enhanced using this optimal photocatalyst.

The dose tuning plays a key role in the photoactivity of nanocomposite photocatalysts due to the upsurging of photoactive sites that are balanced with the adsorbed target molecules and light photons [54–58]. Figure 8a displays the impact of dose alteration (0.7~3.5 g L^{-1}) of 15% Bi_2O_3/CeO_2 on the photocatalytic generation of CH_3OH. The dose-dependent generation of CH_3OH parades the comparative upsurge from 608 ($\pm$19.5) to a maximum of 1300 ($\pm$41.6) µM g^{-1} for 0.7 and 2.8 g L^{-1}, correspondingly, after 9 h of visible-light illumination. This outcome exhibits the improvement of the photocatalytic active spots bared to CO_2 molecules in the case of 2.8 g L^{-1} compared to other doses. Nevertheless, the extra dose of the 15% Bi_2O_3/CeO_2 at 3.5 g L^{-1} decreased the CH_3OH generation to 1230 ($\pm$39.4) µmol g^{-1}. Accordingly, the dosage accumulation could moderately impede the light photons from reaching the photocatalyst's surface, resulting in a reduction of the

overall activity [59,60]. Thus, 2.8 g L^{-1} is the optimized dose for the 15% Bi$_2$O$_3$/CeO$_2$ that exhibits the highest generation rate of CH$_3$OH as described in Figure 8b and proven by chromatograms in Figure S2 (supplementary materials). The spent 15% Bi$_2$O$_3$/CeO$_2$ photocatalyst was also tested for recyclability as presented in Figure 8c. The outcomes showed that the optimal 15% Bi$_2$O$_3$/CeO$_2$ validates five-time reusability for the CO$_2$ reduction under visible light to CH$_3$OH at 1274 μmol g^{-1}, which is 98% of its initial value in the first run. The XRD and TEM investigations for the spent material did not show any significant structural changes (Figure S3, supplemental data). Therefore, the 15% Bi$_2$O$_3$/CeO$_2$ exhibits a workable photocatalytic application for CO$_2$ reduction beneath visible light.

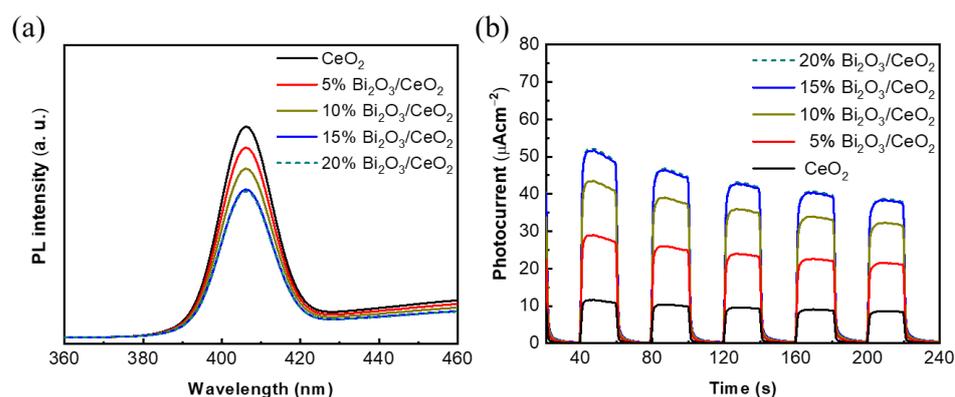**Figure 7.** PL spectra (**a**) and transient photocurrents (**b**) of pure CeO$_2$ and Bi$_2$O$_3$/CeO$_2$ heterojunctions as stated.
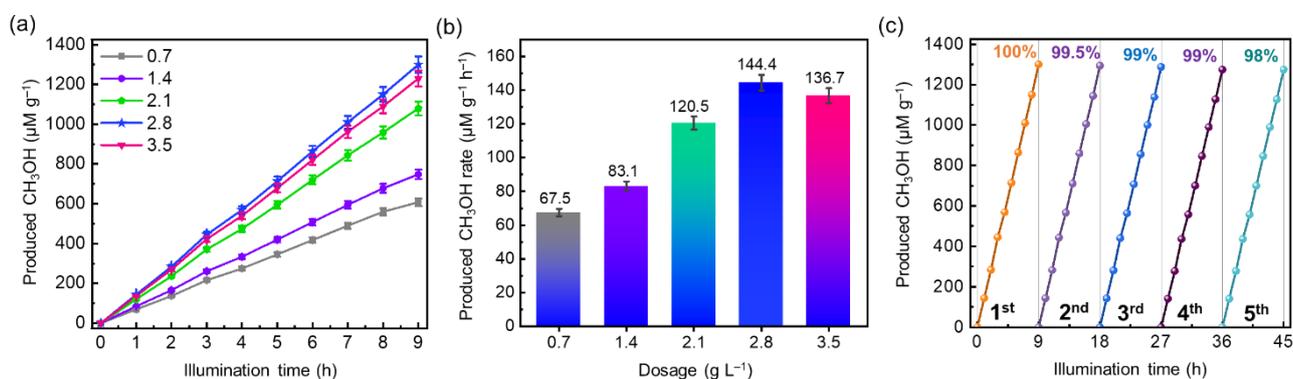

Figure 8. Photocatalytic production of CH$_3$OH over different doses (in g L^{-1}) of 15% Bi$_2$O$_3$/CeO$_2$ heterojunctions as in (**a**). The influence of dosage on the generation rate of produced CH$_3$OH is illustrated in (**b**). The reusability of the best-performing spent photocatalyst dose (2.8 g L^{-1}) is illustrated in (**c**).

Finally, the photoreduction pathway could be proposed as seen in Figure 9 based on previous discussions. The represented band diagrams of p-type Bi$_2$O$_3$ and n-type CeO$_2$ can be calculated by the following formula (supplementary materials S-4):

$$E_{CB} = \chi - E_e - 0.5E_g \tag{1}$$

$$E_{VB} = E_{CB} + E_g \tag{2}$$

where E$_{VB}$ and E$_{CB}$ are the valence (VB) and conduction (CB) band potentials versus the standard hydrogen electrode (NHE), respectively. E$_e$ is the energy of free electrons and χ is the electronegativity of the semiconductor photocatalyst, which is determined in supplementary materials [61–63]. Thus, upon illumination of both semiconductors by visible light, the photoinduced charge carriers, namely electrons (e^-s), are generated at

-0.405 and $+0.535$ eV corresponding to the CB of Bi_2O_3 and CeO_2, respectively, while the holes (h^+s) were located at $+2.525$ and $+2.93$, corresponding to VB of Bi_2O_3 and CeO_2, respectively. Since the p-n heterojunction is formed between p-type Bi_2O_3 and n-type CeO_2, an electric field (signed as E) is designed at the interface of the formed heterojunction and band-bending occurs due to the unified Fermi levels [64–66]. Thus, the excited e^-s at the CB of p-type Bi_2O_3 could recombine with the h^+s left at the VB of n-type CeO_2 by the driving electric field effect [67]. On the other hand, the high redox potential e^-s on the CB of CeO_2 and h^+s on the VB of Bi_2O_3 can contribute to the photoreduction of CO_2 as follows: The H_2 molecules could react with the h^+s resulting in the splitting reaction to protons, oxygen, and free e^-s as shown in Equation (3) [68,69].
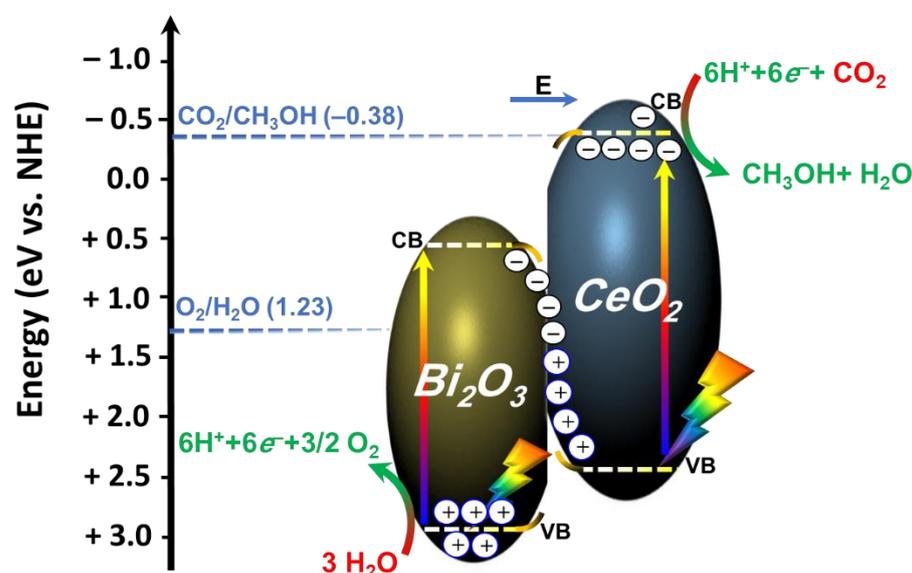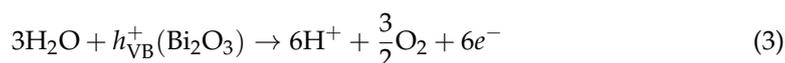
$$3H_2O + h^+_{VB}(Bi_2O_3) \rightarrow 6H^+ + \frac{3}{2}O_2 + 6e^- \tag{3}$$

Figure 9. Estimated band diagrams, charge transfer, and photocatalytic pathway for CO_2 conversion into methanol over optimized Bi_2O_3/CeO_2 heterojunctions.

At last, at the CB of CeO_2, which is very close to the reduction potential of CO_2 into CH_3OH [68,70], the produced protons and e^-s in (3) can selectively convert the CO_2 to CH_3OH as in (4)

$$6e^- + 6H^+ + CO_2 \text{ (CB of } CeO_2) \rightarrow CH_3OH + H_2O \tag{4}$$
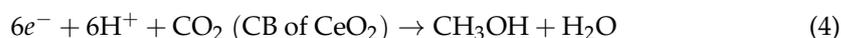
Therefore, the improved, recyclable, and efficient 15% Bi_2O_3/CeO_2 heterojunctions reveal the promoted photoconversion of CO_2 to an alternative renewable fuel under visible-light illumination.

3. Experiments

3.1. Chemicals

All materials were purchased from Merck in this work without subsequent treatment. The Ce and Bi precursors were $Ce(NO_3)_3 \cdot 6H_2O$ (99.999% trace metals basis) and $Bi(NO_3)_3 \cdot 5H_2O$ (99.999% trace metals basis). The polymeric non-ionic surfactant, namely Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic F-108, MW~14,600), was utilized as the growth-limiting reagent and micelle template [71]. Acetic (CH_3COOH, $\geq$99.7%) and hydrochloric (HCl, ACS reagent, 37%) acids were used in the sol-gel process for hydrolysis and esterification procedures. Ethanol absolute (CH_3CH_2OH, $\geq$99.8%) and deionized water (DI-H_2O, >18.2 MΩ) were also used for hy-

drolysis and washing purposes. Sodium carbonate (Na_2CO_3, $\geq$99.5%, ACS reagent) was used as the CO_2 source in the photoreaction system.

3.2. Synthesis of CeO_2 and Bi_2O_3/CeO_2 Photocatalysts

Nanocrystalline CeO_2 particles were synthesized by a modified sol-gel method in the presence of Pluronic F-108. In detail, 2.0 g of F-108 was disseminated in 40 mL of CH_3CH_2OH under vigorous stirring. After that, 12 mmol of HCl and 40 mmol CH_3COOH were progressively poured under the same conditions and then left for 1h. Then, 1.63 g of $Ce(NO_3)_3 \cdot 6H_2O$ was included in the above viscous solution and kept for another 2 h. The cloudy suspended mixture was then transferred into a clean Petri dish for 12 h of polymerization in a humidity chamber operated at 40 °C before drying at 65 °C for another 24 h. The obtained hard gel was crystallized for 5 h at 650 °C to obtain mesostructured CeO_2 nanoparticles. The Bi_2O_3/CeO_2 heterojunctions were prepared by impregnating the Bi_2O_3 into the CeO_2 matrix. In brief, 1.0 g of synthesized CeO_2 was sonicated in 100 mL of CH_3CH_2OH for 10 min. Next, 52 mg of $Bi(NO_3)_3 \cdot 5H_2O$ was familiarized into the solution while stirring and maintained for 1 h. Then, CH_3CH_2OH was evaporated by increasing the temperature to 80 °C. After approximately 5 h, the calcination of the dried powder was performed at 600 °C for 3 h to crystallize the 5% Bi_2O_3/CeO_2 heterojunction. The above procedure was repeated by increasing the Bi^{3+} precursor amount to 104, 156, and 208 mg to obtain 10, 15, and 20% Bi_2O_3/CeO_2 nanocomposites.

3.3. Depictive Characterization of the Obtained CeO_2 and Bi_2O_3/CeO_2

Numerous instruments have been employed to characterize the produced sample. The Bruker AXS D8 X-ray diffraction (XRD, Billerica, MA, USA) unit explored the crystalline phases of the ground powders. The surface composition of the 15% Bi_2O_3/CeO_2 was investigated by the Thermo VG Multilab 2000 X-ray photoelectron spectrometer (XPS, East Grinstead, UK). Regarding the morphology study, a high-resolving-power JEOL-JEM-1230 transmission electron microscope (TEM, Tokyo, Japan) examined the samples dispersed on carbon-coated grids. The Nova Quantachrome analyzer generated N_2 adsorption–desorption (Ostfildern-Scharnhausen, Germany) isotherms to describe the surface texture of the degassed samples at 150 °C. The specific surface area (S_{BET}) was calculated based on the Brunauer–Emmett–Teller (BET) formula, which estimates the specific surface area of the prepared structures. The light harvesting of CeO_2 and Bi_2O_3/CeO_2 was studied via a Jasco spectrophotometer (V-570, Tokyo, Japan) in the 200–800 nm spectral range. The bandgap energy (E_g) was determined based on the modified Tauc formula through their diffusive reflectance. Photoluminescence emission (PL) was investigated by an RF-5301 fluorescence spectrometer (Shimadzu, Kyoto, Tapan) in ambience. Lastly, the electrochemical workstation (Zahner Zennium, Ostfildern-Scharnhausen, Germany) measured the transient photocurrents of the 0.3×0.3 cm^2 working electrodes composed of each sample on Ti foil at zero bias during the ON and OFF states of 1.0 mW cm^{-2} light illumination.

3.4. Setup for Photoreduction of CO_2

The photoreduction experiments were performed in a homemade photoreactor containing a 250 mL two-neck quartz flask. The simulated visible light was provided by a 300 W Xe lamp (Newport, CA, USA, 45.2 mW cm^{-2}) equipped with a 420 nm cut-off filter. In detail, a certain dose of the synthesized photocatalyst was dispersed in 125 mL of H_2O before being heated to 80 °C. Then, 135 mg of Na_2CO_3 was inserted into the above suspension. Moreover, nitrogen gas was initially introduced for 30 min to ensure an inert atmosphere at 100 sccm. After that, 0.315 mL of 4 M HCl was gently injected to generate CO_2. The whole system was kept in murky conditions for 1 h to settle the equilibrium. The photoreactor was then irradiated by visible light. At fixed one-hour intervals, a gas chromatograph (GC-FID, Shimadzu) equipped with a flame ionization detector was employed to sense the formed products through the photoreaction [68]. The produced spectra generated by the detection unit were compared with the standard GC spectra of 2.5 mM L^{-1} CH_3OH

solution (supplementary Figure S1) [21]. The produced CH_3OH was recognized in the above-mentioned spectra under the same experimental conditions using the GC. Generally, neither CH_3OH nor other products are detected before light illumination. The reusability of the spent photocatalyst for five independent cycles was performed via simple drying under ambient conditions for 1 h at 120 °C.

4. Conclusions

A facile sol-gel-based method was applied for the fabrication of the Bi_2O_3/CeO_2 heterojunction photocatalyst. The precise addition of p-type Bi_2O_3 amended the absorbance in the visible light regime through the reduction of the overall bandgap of the produced Bi_2O_3/CeO_2 heterojunction down to 2.74 eV. The various Bi_2O_3-included CeO_2 were applied for the selective photocatalytic reduction of CO_2 into methanol beneath visible light. The 2.8 g L^{-1} dose of 15% Bi_2O_3/CeO_2 generated 1300 μmol/g of CH_3OH within 9 h of illumination, nearly 18.6-fold higher than pure CeO_2. This optimized heterojunction verified the five-time reusability at 98% of its initial performance. The substantial photoactivity of Bi_2O_3/CeO_2 is attributed to the significant photogenerated charge separation in addition to the amended harvesting of light. This work provides plenty of room for the future of renewable fuel production from CO_2 utilizing metal oxide-based heterostructure photocatalysts.

References

1. Plaza, M.G.; Mart, S.; Rubiera, F. CO_2 Capture, Use, and Storage in the Cement Industry: State of the Art and Expectations. *Energies* **2020**, *13*, 5692. [CrossRef]
2. Kang, S.M.; Adhikari, A.; Bhatta, D.; Gam, H.J.; Gim, M.J.; Son, J.I.; Shin, J.Y.; Lee, I.J. Comparison of Effects of Chemical and Food Waste-Derived Fertilizers on the Growth and Nutrient Content of Lettuce (*Lactuca Sativa* L.). *Resources* **2022**, *11*, 21. [CrossRef]
3. Gao, Y.; Zhuang, B.; Wang, T.; Chen, H.; Li, S.; Wei, W.; Lin, H.; Li, M. Climatic–Environmental Effects of Aerosols and Their Sensitivity to Aerosol Mixing States in East Asia in Winter. *Remote Sens.* **2022**, *14*, 3539. [CrossRef]
4. Modarress Fathi, B.; Ansari, A.; Ansari, A. Threats of Internet-of-Thing on Environmental Sustainability by E-Waste. *Sustainability* **2022**, *14*, 161. [CrossRef]
5. Valipour, M.; Bateni, S.M.; Jun, C. Global Surface Temperature: A New Insight. *Climate* **2021**, *9*, 81. [CrossRef]

6. Siddique, R.; Mejia, A.; Mizukami, N.; Palmer, R.N. Impacts of Globalwarming of 1.5, 2.0 and 3.0 °C on Hydrologic Regimes in the Northeastern U.S. *Climate* **2021**, *9*, 9. [CrossRef]

7. Ata, B.; Pakrooh, P.; Barkat, A.; Benhizia, R.; Pénzes, J. Inequalities in Regional Level Domestic CO_2 Emissions and Energy Use: A Case Study of Iran. *Energies* **2022**, *15*, 3902. [CrossRef]

8. Zhang, C.; Zhang, W.; Luo, W.; Gao, X.; Zhang, B. Analysis of Influencing Factors of Carbon Emissions in China's Logistics Industry: A Gdim-Based Indicator Decomposition. *Energies* **2021**, *14*, 5742. [CrossRef]

9. Pires, L.; Vaz, M.; Carolina, A.; De Oliveira, C.; Falcon, L.; Stella, M.; Pimenta, S.; Bessa, I.G.; Wouters, J.; Andrade, H.S.; et al. Capture and Reuse of Carbon Dioxide (CO_2) for a Plastics Circular Economy: A Review. *Processes* **2021**, *9*, 759. [CrossRef]

10. Catizzone, E.; Bonura, G.; Migliori, M.; Frusteri, F.; Giordano, G. CO_2 Recycling to Dimethyl Ether: State-of-the-Art and Perspectives. *Molecules* **2018**, *23*, 31. [CrossRef]

11. Nebel, A.; Cantor, J.; Salim, S.; Salih, A.; Patel, D. The Role of Renewable Energies, Storage and Sector-Coupling Technologies in the German Energy Sector under Different CO_2 Emission Restrictions. *Sustainability* **2022**, *14*, 10379. [CrossRef]

12. Sarkar, M.; Chung, B. Do Effect of Renewable Energy to Reduce Carbon Emissions under a Flexible Production System: A Step toward Sustainability. *Energies* **2021**, *14*, 215. [CrossRef]

13. Materials, M. Supercritical CO_2 Curing of Resource-Recycling Secondary Main Materials. *Materials* **2022**, *15*, 4581.

14. Hussain, S.; Wang, Y.; Guo, L.; He, T. Theoretical Insights into the Mechanism of Photocatalytic Reduction of CO_2 over Semiconductor Catalysts. *J. Photochem. Photobiol. C Photochem. Rev.* **2022**, *52*, 100538. [CrossRef]

15. Jerome, M.P.; Alahmad, F.A.; Salem, M.T.; Tahir, M. Layered Double Hydroxide (LDH) Nanomaterials with Engineering Aspects for Photocatalytic CO_2 conversion to Energy Efficient Fuels: Fundamentals, Recent Advances, and Challenges. *J. Environ. Chem. Eng.* **2022**, *10*, 108151. [CrossRef]

16. Sundar, D.; Karuppasamy, L.; Gurusamy, L.; Liu, C.H.; Wu, J.J. Perovskites-like Composites for CO_2 Photoreduction into Hydrocarbon Fuels. *Curr. Opin. Green Sustain. Chem.* **2022**, *33*, 100563. [CrossRef]

17. Kumar, A.; Singh, P.; Khan, A.A.P.; Van Le, Q.; Nguyen, V.H.; Thakur, S.; Raizada, P. CO_2 Photoreduction into Solar Fuels via Vacancy Engineered Bismuth-Based Photocatalysts: Selectivity and Mechanistic Insights. *Chem. Eng. J.* **2022**, *439*, 135563. [CrossRef]

18. Zhang, Z.; Wang, Y.; Cui, G.; Liu, H.; Abanades, S.; Lu, H. Improvement of CO_2 Photoreduction Efficiency by Process Intensification. *Catalysts* **2021**, *11*, 912. [CrossRef]

19. Ali, S.; Flores, M.C.; Razzaq, A.; Sorcar, S.; Hiragond, C.B.; Kim, H.R.; Park, Y.H.; Hwang, Y.; Kim, H.S.; Kim, H.; et al. Gas Phase Photocatalytic CO_2 Reduction, "a Brief Overview for Benchmarking". *Catalysts* **2019**, *9*, 727. [CrossRef]

20. Vega-Mendoza, M.S.; Luévano-Hipólito, E.; Torres-Martínez, L.M. Design and Fabrication of Photocatalytic Coatings with α/β-Bi_2O_3 and Recycled-Fly Ash for Environmental Remediation and Solar Fuel Generation. *Ceram. Int.* **2021**, *47*, 26907–26918. [CrossRef]

21. Liu, Y.; Ji, G.; Dastageer, M.A.; Zhu, L.; Wang, J.; Zhang, B.; Chang, X.; Gondal, M.A. Highly-Active Direct Z-Scheme Si/TiO_2 Photocatalyst for Boosted CO_2 Reduction into Value-Added Methanol. *RSC Adv.* **2014**, *4*, 56961–56969. [CrossRef]

22. Low, J.; Cheng, B.; Yu, J. Surface Modification and Enhanced Photocatalytic CO_2 Reduction Performance of TiO_2: A Review. *Appl. Surf. Sci.* **2017**, *392*, 658–686. [CrossRef]

23. Tang, T.; Yin, Z.; Chen, J.; Zhang, S.; Sheng, W.; Wei, W.; Xiao, Y.; Shi, Q.; Cao, S. Novel P-n Heterojunction Bi_2O_3/Ti_{3+}-TiO_2 Photocatalyst Enables the Complete Removal of Tetracyclines under Visible Light. *Chem. Eng. J.* **2021**, *417*, 128058. [CrossRef]

24. Zhang, X.; Kim, D.; Yan, J.; Lee, L.Y.S. Photocatalytic CO_2 Reduction Enabled by Interfacial S-Scheme Heterojunction between Ultrasmall Copper Phosphosulfide and g-C_3N_4. *ACS Appl. Mater. Interfaces* **2021**, *13*, 9762–9770. [CrossRef] [PubMed]

25. Mohamed, R.M.; Harraz, F.A.; Mkhalid, I.A. Hydrothermal Synthesis of Size-Controllable Yttrium Orthovanadate (YVO_4) Nanoparticles and Its Application in Photocatalytic Degradation of Direct Blue Dye. *J. Alloys Compd.* **2012**, *532*, 55–60. [CrossRef]

26. Mohamed, R.M.; Mkhalid, I.A. Visible Light Photocatalytic Degradation of Cyanide Using Au-TiO_2/Multi-Walled Carbon Nanotube Nanocomposites. *J. Ind. Eng. Chem.* **2015**, *22*, 390–395. [CrossRef]

27. Ismail, A.A.; Ibrahim, I.A.; Mohamed, R.M. Sol-Gel Synthesis of Vanadia-Silica for Photocatalytic Degradation of Cyanide. *Appl. Catal. B Environ.* **2003**, *45*, 161–166. [CrossRef]

28. Wang, Z.; Cheng, B.; Zhang, L.; Yu, J.; Tan, H. BiOBr/NiO S-Scheme Heterojunction Photocatalyst for CO_2 Photoreduction. *Sol. RRL* **2022**, *6*, 2100587. [CrossRef]

29. Mokhtar, M.; Shawky, A. Enhanced Visible-Light-Driven H_2 Evolution over Sol-Gel Prepared Nd_2O_3 Supported with PtO Nanoparticles. *Ceram. Int.* **2022**, *48*, 36670–36677. [CrossRef]

30. Sharma, A.; Hosseini-bandegharaei, A.; Kumar, N.; Kumar, S. Insight into ZnO/Carbon Hybrid Materials for Photocatalytic Reduction of CO_2: An in-Depth Review. *J. CO_2 Util.* **2022**, *65*, 102205. [CrossRef]

31. Bathla, A.; Lee, J.; Younis, S.A.; Kim, K.H. Recent Advances in Photocatalytic Reduction of CO_2 by TiO_2– and MOF–Based Nanocomposites Impregnated with Metal Nanoparticles. *Mater. Today Chem.* **2022**, *24*, 100870. [CrossRef]

32. Kadi, M.W.; Mohamed, R.M. Promoted Photocatalytic Hydrogen Evolution over Core-Shellstructured CO_3O_4/TiO_2 under Visible Light. *Int. J. Mater. Technol. Innov.* **2021**, *1*, 1–13.

33. Allam, N.; El-Shazly, A.; Hegazy, A.; Hamza, M.; El Shenawy, E. The Synergetic Effect of Cobalt Content on Enhancing the Photoelectrochemical Hydrogen Production Performance of In-Situ-Doped TiO_2 Photocatalysts. *Int. J. Mater. Technol. Innov.* **2022**, *2*, 20–28. [CrossRef]

34. Jiang, Z.; Cheng, B.; Zhang, Y.; Wageh, S.; Al-Ghamdi, A.A.; Yu, J.; Wang, L. S-Scheme ZnO/WO$_3$ Heterojunction Photocatalyst for Efficient H$_2$O$_2$ Production. *J. Mater. Sci. Technol.* **2022**, *124*, 193–201. [CrossRef]
35. Li, J.; Zhang, M.; Guan, Z.; Li, Q.; He, C.; Yang, J. Synergistic Effect of Surface and Bulk Single-Electron-Trapped Oxygen Vacancy of TiO$_2$ in the Photocatalytic Reduction of CO$_2$. *Appl. Catal. B Environ.* **2017**, *206*, 300–307. [CrossRef]
36. Zou, Z.; Xie, C.; Zhang, S.; Yu, X.; Zou, T.; Li, J. Preparation and Photocatalytic Activity of TiO$_2$/CeO$_2$/Bi$_2$O$_3$ Composite for Rhodamine B Degradation under Visible Light Irradiation. *J. Alloys Compd.* **2013**, *581*, 385–391. [CrossRef]
37. Hezam, A.; Namratha, K.; Drmosh, Q.A.; Yamani, Z.H.; Byrappa, K. Synthesis of Heterostructured Bi$_2$O$_3$–CeO$_2$–ZnO Photocatalyst with Enhanced Sunlight Photocatalytic Activity. *Ceram. Int.* **2017**, *43*, 5292–5301. [CrossRef]
38. Sabzehmeidani, M.M.; Karimi, H.; Ghaedi, M. Nanofibers Based Quaternary CeO$_2$/CO$_3$O$_4$/Ag/Ag3PO$_4$ S-Scheme Heterojunction Photocatalyst with Enhanced Degradation of Organic Dyes. *Mater. Res. Bull.* **2022**, *147*, 111629. [CrossRef]
39. Zhao, Y.; Lin, C.; Zhang, L.; Meng, X.; Tang, H. Bi$_2$O$_3$ Induced Tremella-like Bi$_2$WO$_6$ with Visible Light Catalytic Performance. *Ceram. Int.* **2022**, *48*, 4584–4594. [CrossRef]
40. He, W.; Wei, Y.; Xiong, J.; Tang, Z.; Wang, Y.; Wang, X.; Deng, J.; Yu, X.; Zhang, X.; Zhao, Z. Boosting Selective Photocatalytic CO$_2$ Reduction to CO over Dual-Core@shell Structured Bi$_2$O$_3$/Bi$_2$WO$_6$@g-C$_3$N$_4$ Catalysts with Strong Interaction Interface. *Sep. Purif. Technol.* **2022**, *300*, 121850. [CrossRef]
41. Hezam, A.; Namratha, K.; Drmosh, Q.A.; Ponnamma, D.; Wang, J.; Prasad, S.; Ahamed, M.; Cheng, C.; Byrappa, K. CeO$_2$ Nanostructures Enriched with Oxygen Vacancies for Photocatalytic CO$_2$ Reduction. *ACS Appl. Nano Mater.* **2020**, *3*, 138–148. [CrossRef]
42. Xu, L.; Zeng, J.; Li, Q.; Luo, X.; Chen, T.; Liu, J.; Wang, L.L. Multifunctional Silicene/CeO$_2$ Heterojunctions: Desirable Electronic Material and Promising Water-Splitting Photocatalyst. *Chin. Chem. Lett.* **2022**, *33*, 3947–3950. [CrossRef]
43. Cui, Z.; Zhang, D.; Hu, J.; Fang, C. CdS/CeO$_2$ Heterostructures as Visible-Light Photocatalysts for the Reduction of Nitro to Amine Organics. *J. Alloys Compd.* **2021**, *885*, 160961. [CrossRef]
44. Wu, D.; Zhang, X.; Liu, S.; Ren, Z.; Xing, Y.; Jin, X.; Ni, G. Fabrication of a Z-Scheme CeO$_2$/Bi$_2$O$_4$ Heterojunction Photocatalyst with Superior Visible-Light Responsive Photocatalytic Performance. *J. Alloys Compd.* **2022**, *909*, 164671. [CrossRef]
45. Hsieh, S.H.; Manivel, A.; Lee, G.J.; Wu, J.J. Synthesis of Mesoporous Bi$_2$O$_3$/CeO$_2$ Microsphere for Photocatalytic Degradation of Orange II Dye. *Mater. Res. Bull.* **2013**, *48*, 4174–4180. [CrossRef]
46. Cui, S.; Ma, Q.; Chen, H.; Zhang, Y.; Sun, F. Heterojunction G-C$_3$N$_4$/CeO$_2$/Bi$_2$O$_3$ Composite for the Photocatalytic Purification of Exhaust Gas. *Mater. Chem. Phys.* **2022**, *285*, 126081. [CrossRef]
47. Nie, J.; Zhu, G.; Zhang, W.; Gao, J.; Zhong, P.; Xie, X.; Huang, Y.; Hojamberdiev, M. Oxygen Vacancy Defects-Boosted Deep Oxidation of NO by β-Bi$_2$O$_3$/CeO$_2$-δ p-n Heterojunction Photocatalyst in Situ Synthesized from Bi/Ce(CO$_3$)(OH) Precursor. *Chem. Eng. J.* **2021**, *424*, 130327. [CrossRef]
48. Yang, X.; Zhang, Y.; Wang, Y.; Xin, C.; Zhang, P.; Liu, D.; Mamba, B.B.; Kefeni, K.K.; Kuvarega, A.T.; Gui, J. Hollow β-Bi$_2$O$_3$@CeO$_2$ Heterostructure Microsphere with Controllable Crystal Phase for Efficient Photocatalysis. *Chem. Eng. J.* **2020**, *387*, 124100. [CrossRef]
49. Masula, K.; Bhongiri, Y.; Raghav Rao, G.; Vijay Kumar, P.; Pola, S.; Basude, M. Evolution of Photocatalytic Activity of CeO$_2$–Bi$_2$O$_3$ Composite Material for Wastewater Degradation under Visible-Light Irradiation. *Opt. Mater.* **2022**, *126*, 112201. [CrossRef]
50. Li, X.; Guan, J.; Jiang, H.; Song, X.; Huo, P.; Wang, H. RGO Modified R-CeO$_2$/g-C$_3$N$_4$ Multi-Interface Contact S-Scheme Photocatalyst for Efficient CO$_2$ Photoreduction. *Appl. Surf. Sci.* **2021**, *563*, 150042. [CrossRef]
51. Li, L.; Yan, B. CeO$_2$-Bi$_2$O$_3$ Nanocomposite: Two Step Synthesis, Microstructure and Photocatalytic Activity. *J. Non Cryst. Solids* **2009**, *355*, 776–779. [CrossRef]
52. Albukhari, S.M.; Shawky, A. Ag/Ag$_2$O-Decorated Sol-Gel-Processed TeO$_2$ Nanojunctions for Enhanced H$_2$ Production under Visible Light. *J. Mol. Liq.* **2021**, *336*, 116870. [CrossRef]
53. Prajapati, P.K.; Malik, A.; Nandal, N.; Pandita, S.; Singh, R.; Bhandari, S.; Saran, S.; Jain, S.L. Morphology Controlled Fe and Ni-Doped CeO$_2$ Nanorods as an Excellent Heterojunction Photocatalyst for CO$_2$ Reduction. *Appl. Surf. Sci.* **2022**, *588*, 152912. [CrossRef]
54. Kadi, M.W.; Mohamed, R.M.; Ismail, A.A.; Bahnemann, D.W. Soft and Hard Templates Assisted Synthesis Mesoporous CuO/g-C$_3$N$_4$ Heterostructures for Highly Enhanced and Accelerated Hg(II) Photoreduction under Visible Light. *J. Colloid Interface Sci.* **2020**, *580*, 223–233. [CrossRef]
55. Kadi, M.W.; Mohamed, R.M.; Ismail, A.A.; Bahnemann, D.W. Performance of Mesoporous α-Fe$_2$O$_3$/g-C$_3$N$_4$ Heterojunction for Photoreduction of Hg(II) under Visible Light Illumination. *Ceram. Int.* **2020**, *46*, 23098–23106. [CrossRef]
56. Kadi, M.W.; Mohamed, R.M.; Ismail, A.A.; Bahnemann, D.W. Decoration of G-C$_3$N$_4$ Nanosheets by Mesoporous CoFe$_2$O$_4$ Nanoparticles for Promoting Visible-Light Photocatalytic Hg(II) Reduction. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *603*, 125206. [CrossRef]
57. Shawky, A.; Alhaddad, M.; Al-Namshah, K.S.; Mohamed, R.M.; Awwad, N.S. Synthesis of Pt-Decorated CaTiO$_3$ Nanocrystals for Efficient Photoconversion of Nitrobenzene to Aniline under Visible Light. *J. Mol. Liq.* **2020**, *304*, 112704. [CrossRef]
58. Mohamed, R.M.; Shawky, A. CNT Supported Mn-Doped ZnO Nanoparticles: Simple Synthesis and Improved Photocatalytic Activity for Degradation of Malachite Green Dye under Visible Light. *Appl. Nanosci.* **2018**, *8*, 1179–1188. [CrossRef]
59. Mohamed, R.M.; McKinney, D.; Kadi, M.W.; Mkhalid, I.A.; Sigmund, W. Platinum/Zinc Oxide Nanoparticles: Enhanced Photocatalysts Degrade Malachite Green Dye under Visible Light Conditions. *Ceram. Int.* **2016**, *42*, 9375–9381. [CrossRef]

60. Kadi, M.W.; McKinney, D.; Mohamed, R.M.; Mkhalid, I.A.; Sigmund, W. Fluorine Doped Zinc Oxide Nanowires: Enhanced Photocatalysts Degrade Malachite Green Dye under Visible Light Conditions. *Ceram. Int.* **2016**, *42*, 4672–4678. [CrossRef]
61. Rajendran, S.; Khan, M.M.; Gracia, F.; Qin, J.; Gupta, V.K.; Arumainathan, S. Ce_{3+}-Ion-Induced Visible-Light Photocatalytic Degradation and Electrochemical Activity of ZnO/CeO_2 Nanocomposite. *Sci. Rep.* **2016**, *6*, 1–11. [CrossRef] [PubMed]
62. Channei, D.; Chansaenpak, K.; Phanichphant, S.; Jannoey, P.; Khanitchaidecha, W.; Nakaruk, A. Synthesis and Characterization of WO_3/CeO_2 Heterostructured Nanoparticles for Photodegradation of Indigo Carmine Dye. *ACS Omega* **2021**, *6*, 19771–19777. [CrossRef] [PubMed]
63. Basaleh, A.S.; Shawky, A.; Zaki, Z.I. Visible Light-Driven Photodegradation of Ciprofloxacin over Sol-Gel Prepared Bi_2O_3-Modified La-Doped $NaTaO_3$ Nanostructures. *Ceram. Int.* **2021**, *47*, 19205–19212. [CrossRef]
64. Shawky, A.; Mohamed, R.M. S-Scheme Heterojunctions: Emerging Designed Photocatalysts toward Green Energy and Environmental Remediation Redox Reactions. *J. Environ. Chem. Eng.* **2022**, *10*, 108249. [CrossRef]
65. Zhang, L.; Zhang, J.; Yu, H.; Yu, J. Emerging S-Scheme Photocatalyst. *Adv. Mater.* **2022**, *34*, 2107668. [CrossRef]
66. Xu, Q.; Zhang, L.; Cheng, B.; Fan, J.; Yu, J. S-Scheme Heterojunction Photocatalyst. *Chem* **2020**, *6*, 1543–1559. [CrossRef]
67. Shawky, A.; Mohamed, R.M.; Alahmadi, N.; Zaki, Z.I. Enhanced Photocatalytic Reduction of Hexavalent Chromium Ions over S-Scheme Based 2D MoS_2-Supported TiO_2 Heterojunctions under Visible Light. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *641*, 128564. [CrossRef]
68. Alhaddad, M.; Shawky, A. Pt-Decorated $ZnMn_2O_4$ Nanorods for Effective Photocatalytic Reduction of CO_2 into Methanol under Visible Light. *Ceram. Int.* **2021**, *47*, 9763–9770. [CrossRef]
69. Lais, A.; Gondal, M.A.; Dastageer, M.A. Semiconducting Oxide Photocatalysts for Reduction of CO_2 to Methanol. *Environ. Chem. Lett.* **2018**, *16*, 183–210. [CrossRef]
70. Pocoví-Martínez, S.; Zumeta-Dube, I.; Diaz, D. Production of Methanol from Aqueous CO_2 by Using Co_3O_4 Nanostructures as Photocatalysts. *J. Nanomater.* **2019**, *2019*, 1–10. [CrossRef]
71. Pal, N.; Lee, J.H.; Cho, E.B. Recent Trends in Morphology-Controlled Synthesis and Application of Mesoporous Silica Nanoparticles. *Nanomaterials* **2020**, *10*, 2122. [CrossRef] [PubMed]