Enhanced Photocatalytic CO₂ Reduction in Defect-Engineered Z-Scheme WO₃ₓ/g-C₃N₄ Heterostructures

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Supporting Information

ABSTRACT: Oxygen vacancy-modified WO₃ₓ nanorods composited with g-C₃N₄ have been synthesized via the chemisorption method. The crystalline structure, morphology, composition, band structure, and charge separation mechanism for WO₃ₓ/g-C₃N₄ heterostructures are studied in detail. The g-C₃N₄ nanosheets are attached on the surface of WO₃ₓ nanorods. The Z-scheme separation is confirmed by the analysis of generated hydroxyl radicals. The electrons in the lowest unoccupied molecular orbital of g-C₃N₄ and the holes in the valence band of WO₃ can participate in the photocatalytic reaction to reduce CO₂ into CO. New energy levels of oxygen vacancies on the interface of heterostructures, such as visible-light response, separation behaviors of charge carriers, and lifetime of photogenerated electrons, is rarely reported.

Herein, defect-engineered WO₃ₓ nanorods are prepared by vacuum thermal treatment and WO₃ₓ/g-C₃N₄ heterostructures are synthesized through a chemisorption method. The morphology structure, band structure, and separation of electrons and holes are investigated systematically. These WO₃ₓ/g-C₃N₄ heterostructures exhibit a significantly improved catalytic activity for reduction of CO₂ into CO compared to pristine g-C₃N₄, WO₃, and WO₃₈/g-C₃N₄. The introduced oxygen vacancies would create defect energy levels below the conduction band of WO₃ and facilitate the separation of charge carriers in Z-scheme pathway. This work provides insights into practical applications of Z-scheme heterostructures toward efficient photocatalytic CO₂ reduction.

2. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of pure WO₃, WO₃₈, and W₈C3 (the abbreviations of WO₃ₓ/g-C₃N₄, and the nominal weight ratio of g-C₃N₄ to WO₃ₓ is 3%).
Figure 1. XRD patterns of pure WO₃, WO₃₋ₓ, and WₓC₃ samples and g-C₃N₄.

samples and g-C₃N₄. Two diffraction peaks at 13.1 and 27.4° are found for g-C₃N₄ samples, corresponding to the (001) and (002) planes (JCPDS No. 87-1526). For pure WO₃, only two obvious diffraction peaks at 23.0 and 46.9° are observed, ascribed to the (001) and (002) planes of WO₃, respectively (JCPDS No. 20-1324). Compared to the standard diffraction data of WO₃, no other diffraction peaks are observed. The peak of (001) plane is significantly sharp, suggesting that the WO₃ crystals grow preferentially along the c axis direction. The XRD pattern of WO₃₋ₓ is almost the same as that of pure WO₃, suggesting that the vacuum thermal treatment does not change the crystal structure of WO₃₋ₓ samples. After the compositing process, the XRD patterns of WₓC₃ are almost the same as those of pure WO₃ and WO₃₋ₓ samples. No additional peaks related to g-C₃N₄ are detected, which is probably due to the relative low weight ratio of g-C₃N₄.

The morphologies of the as-prepared nanostructures (WC₃ (the abbreviations of WₓC₃/g-C₃N₄, and the nominal weight ratio of g-C₃N₄ to Wₓ, is 3%) and WₓC₃) are shown in Figure 2. As shown in the transmission electron microscopy (TEM) image in Figure 2a, the WC₃ samples are composed of crystallized nanorods with a uniform diameter of approximately 10 nm and length of 50–100 nm. It is observed from the high-resolution transmission electron microscopy (HRTEM) image in Figure 2b that some WO₃ nanorods are compositcd with g-C₃N₄ (TEM of pristine g-C₃N₄ shown in Figure S1). In addition, the lattice fringe is 0.39 nm corresponding to the (001) plane of WO₃ (JCPDS No. 20-1324), which suggests that the growth of the WO₃ nanorods is along the [001] direction. After the vacuum thermal treatment (Figure 2c,d), the morphology of the nanorods remains almost unchanged and the WO₃₋ₓ nanorods are still compositcd with g-C₃N₄. These TEM results are in good agreement with the XRD results.

X-ray photoelectron spectroscopy (XPS) images are provided in Figure 3 to investigate the chemical states of W, O, C, and N atoms. Figure 3a shows the XPS C 1s spectra of the pure WO₃, WₓC₃, and g-C₃N₄ samples. For all samples, the peaks centered at 284.8 eV are ascribed to the surface adsorbed C atoms that can be used for calibration.²⁵ For the g-C₃N₄ sample, in addition to the C 1s peak at 284.8 eV, a new peak at approximately 288.1 eV is detected, corresponding to the C atoms in –N–C–N– coordination for g-C₃N₄. For WₓC₃ samples, a weak peak centered at approximately 288.6 eV is also found, suggesting the existence of g-C₃N₄. For the XPS N 1s spectra (Figure 3b), the major peaks at approximately 398.7 eV for g-C₃N₄ and 399.1 eV for WₓC₃ are ascribed to the sp² bonding N atoms in –C–N–C– structures.²⁶ The small difference for the C 1s and N 1s spectra of WₓC₃ and g-C₃N₄, respectively, is caused by the heterojunction between g-C₃N₄ and Wₓ. The chemical interaction between g-C₃N₄ and WO₃₋ₓ such as the Mo–N bond, improves the electron transfer process in the WₓC₃ heterojunction. For the XPS W 4f spectrum (Figure 3c), the double peaks at approximately 35.9 and 38.1 eV are attributed to the W 4f⁷/₂ and W 4f⁵/₂ of W²⁺ ions in WO₃, respectively.⁶,⁷ Moreover, two different valence states of W ions can be observed for WₓC₃ samples. In addition to the peaks of W²⁺ ions, the new double peak at 35.5 and 37.7 eV can be observed, ascribed to the W 4f⁷/₂ and W 4f⁵/₂ of W³⁺ ions, respectively.¹⁹,²³ The existence of W³⁺ is usually considered as a direct evidence for the existence of oxygen vacancies in the WO₃ system.¹⁸,¹⁹ The XPS O 1s spectra of WO₃ and WₓC₃ are deconvoluted into two peaks, as shown in Figure 3d. One peak at 530.9 eV is ascribed to the lattice O in WO₃, and the other peak at 531.9 eV is ascribed to the surface adsorbed O species. Compared to WO₃, the XPS O 1s peak for the WₓC₃ sample shifts to a lower binding energy by 0.1 eV, which is due to the change of chemical states from W²⁺ to W³⁺.²⁵ This XPS analysis confirms that the oxygen vacancies are successfully introduced into WO₃ via the vacuum thermal treatment and the WO₃₋ₓ/g-C₃N₄ heterojunction is formed. Moreover, the peak intensity of the electron spin resonance (ESR) signal at g = 2.002 increases in WₓC₃, compared to that in WC₃ (Figure S2), which also confirms that oxygen vacancies are introduced into WO₃ nanorods after the vacuum thermal treatment.

To evaluate the photocatalytic performance of the as-prepared photocatalyst, the photoreduction of CO₂ with H₂O into CO is shown in Figure 4. Both WO₃ and g-C₃N₄ samples exhibit poor photocatalytic activities, with only 1.11 and 0.92 μmol of CO detected after 8 h irradiation, respectively, which are almost the same as the blank experiment (0.49 μmol). The WO₃₋ₓ samples also exhibit a limited photocatalytic activity (1.39 μmol). A series of WₓC₃ samples all exhibit enhanced photocatalytic activities. The WC₃ sample exhibits the best photocatalytic performance among all samples (Figure S3). There is 5.17 μmol of CO produced after 8 h irradiation. The photocatalytic performance is further enhanced for WₓC₃ samples, and 6.64 μmol CO is detected for 8 h irradiation. These results suggest that the introduction of oxygen vacancies into the interface between g-C₃N₄ and WO₃ is an effective method to improve the photocatalytic activity.
Figure 5a shows the photoluminescence (PL) spectra of g-C3N4, WC3, and WxC3 samples to investigate the influence of oxygen vacancies at the interface of WO3−x and g-C3N4 on the behaviors of photogenerated charge carriers. The g-C3N4 sample exhibits the highest emission intensity among all samples, indicating the fast recombination of photogenerated electrons and holes. After the g-C3N4 is compositied with WO3 nanorods (WC3 and WxC3), the PL intensity is quenched efficiently, suggesting an efficient separation of charge carriers at the interface of g-C3N4 and WO3. The electrons in the conduction band of WO3 might combine with the holes in highest occupied molecular orbital (HOMO) levels of g-C3N4, suppressing the recombination of charge carriers. Furthermore, it is noted that the PL intensity for WxC3 slightly decreases compared to that of WC3, implying that the oxygen vacancies in WO3 can further promote the separation of charge carriers. The electrons in the energy levels of oxygen vacancies might recombine with the holes in HOMO levels of g-C3N4, further separating the charge carriers.

Time-resolved PL decay curve is a sensitive and powerful method to further study the separation behaviors of charge carriers.

Figure 4. Photocatalytic activity for reduction of CO2 into CO of pure g-C3N4, WO3, WO3−x, WC3, and WxC3 samples under a xenon lamp for 8 h.

Figure 5a shows the photoluminescence (PL) spectra of g-C3N4, WC3, and WxC3 samples to investigate the influence of oxygen vacancies at the interface of WO3−x and g-C3N4 on the behaviors of photogenerated charge carriers. The g-C3N4 sample exhibits the highest emission intensity among all samples, indicating the fast recombination of photogenerated electrons and holes. After the g-C3N4 is compositied with WO3 nanorods (WC3 and WxC3), the PL intensity is quenched efficiently, suggesting an efficient separation of charge carriers at the interface of g-C3N4 and WO3. The electrons in the conduction band of WO3 might combine with the holes in highest occupied molecular orbital (HOMO) levels of g-C3N4, suppressing the recombination of charge carriers. Furthermore, it is noted that the PL intensity for WxC3 slightly decreases compared to that of WC3, implying that the oxygen vacancies in WO3 can further promote the separation of charge carriers. The electrons in the energy levels of oxygen vacancies might recombine with the holes in HOMO levels of g-C3N4, further separating the charge carriers.

Time-resolved PL decay curve is a sensitive and powerful method to further study the separation behaviors of charge carriers.

Figure 5. Photoluminescence spectra (a) and time-resolved PL decay curves (b) for WC3 and WxC3 samples.
carriers. As shown in Figure 5b, the fast decay lifetime ($\tau_1$) is usually related to the nonradiative relaxation process and the longer decay lifetime ($\tau_2$) is related to the radiative process, arising from the recombination of photogenerated electrons and holes. The values of $\tau_1$ and $\tau_2$ for WC3 and W$_C$3 are calculated by double exponential decay fitting. The $\tau_2$ value for W$_C$3 is 6.29 ns, which is much longer than that for WC3 (3.91 ns). This result suggests that the introduction of oxygen vacancies on the surface of WO$_3$ can prolong the lifetime of charge carriers in the WO$_3$/$g$-C$_3$N$_4$ heterojunction. The photogenerated electrons in WO$_3$ would be trapped in the energy levels of oxygen vacancies and further combine with the holes in HOMO levels of g-C$_3$N$_4$. It becomes difficult for the electrons to stay in the lowest unoccupied molecular orbital (LUMO) levels of g-C$_3$N$_4$ to recombine with the holes. A similar reason can be applied to the holes in the valence band of WO$_3$. Therefore, the lifetime of the charge carriers for W$_C$3 is prolonged, which is in favor of the photocatalytic performance eventually.

Moreover, the photocurrent responses of WC3 and W$_C$3 are illustrated in Figure S4. The photocurrent densities for WC3 and W$_C$3 are much higher than those of WC3, which is in good agreement with the photocatalytic results. This observation confirms that the introduction of the oxygen vacancies on the surface of WO$_3$ can enhance the visible-light response and facilitate the separation of charge carriers of the WO$_3$/$g$-C$_3$N$_4$ heterojunction. The detailed photocatalytic mechanism will be discussed in the following section.

The diffuse reflectance UV–visible (UV–vis) absorption spectra of g-C$_3$N$_4$, WO$_3$, WO$_{3-x}$, and W$_C$3 nanorods are plotted in Figure 6a. Pure WO$_3$ samples show strong absorption in the UV light region and also exhibit some absorption from 400 to 550 nm. For WO$_{3-x}$ samples, the absorption edge is almost the same as that of pure WO$_3$, suggesting that the vacuum thermal treatment can hardly change the band gap of WO$_3$. However, a broad peak from 400 to 800 nm is observed for WO$_{3-x}$ samples, whose absorption maximum is at approximately 523 nm. It has been reported that the oxygen vacancies would induce defect energy levels below the conduction band of WO$_3$. Thus, the enhancement of visible-light response can be ascribed to the electron transition from the valence band to energy levels of oxygen vacancies. On the other hand, g-C$_3$N$_4$ shows a strong absorption, ascribed to the electron transition from the HOMO levels to the LUMO levels. The maximum of absorption peak of g-C$_3$N$_4$ is also at approximately 420 nm. After WO$_{3-x}$ is composited with g-C$_3$N$_4$, a red shift is observed for the absorption edge and the absorption around 420 nm is enhanced for the W$_C$3 samples.

The band gap of semiconductors can be determined by the following Tauc equation

$$a\nu \nu = A(\nu - E_g)^n$$

where $\alpha$ is the absorption coefficient, $\nu$ is the Planck’s constant, $\nu$ is the frequency, $A$ is the proportionality, and $E_g$ is the band gap. $n$ is 1/2 for direct band gap semiconductors and 2 for indirect band gap semiconductors. In this work, WO$_3$ is a direct band gap semiconductor and g-C$_3$N$_4$ is an indirect band gap semiconductor. Hence, $n$ is 2 for g-C$_3$N$_4$ and 1/2 for WO$_3$. As shown in Figure 6b, the corresponding band gaps of g-C$_3$N$_4$ and WO$_3$ are estimated to be 2.62 and 3.17 eV. The band gap of WO$_3$ in this work is larger than that from previous reports which may be caused by the ultrathin diameter of nanorods. After the introduction of oxygen vacancies, the band gap of WO$_{3-x}$ nanorods remains as 3.17 eV. The direct band gap for W$_C$3 is narrowed to 3.05 eV, corresponding to the red shift of the absorption edge. As the absorption maximum of the tailed peak for WO$_{3-x}$ samples originating from oxygen vacancies is around 523 nm, the energy level of oxygen vacancies is deduced to be approximately 0.8 eV below the conduction band minimum (CBM) of WO$_3$.

The Mott–Schottky analysis revealed that the flat band potentials of WC3, W$_C$3, and g-C$_3$N$_4$ are plotted in Figure 7. The valence band maximum of WO$_3$ is approximately 3.20 eV (+2.80 eV, vs normal hydrogen electrode (NHE)), and the HOMO level for g-C$_3$N$_4$ is at approximately 2.05 eV (+1.65 eV, vs NHE). Moreover, the valence bands of WO$_{3-x}$ and W$_C$3 samples are almost the

![Figure 6](image6.png)

Figure 6. (a) Diffuse reflectance UV–vis absorption spectra and (b) corresponding Tauc plots of g-C$_3$N$_4$, WO$_3$, WO$_{3-x}$, and W$_C$3 samples.
same as that of pure WO\textsubscript{3}. According to the discussion above, the corresponding band gaps of WO\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4} are estimated to be 3.17 and 2.62 eV. Therefore, the LUMO levels and the conduction band minimum for g-C\textsubscript{3}N\textsubscript{4} and WO\textsubscript{3} are estimated to be at −0.97 and −0.37 eV (vs NHE), respectively.

Based on the discussion above, the schematic diagram of the band structure for WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} heterostructures can be plotted in Figure S5. For WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} heterostructures, there are two possible pathways to separate charge carriers, namely, typical heterostructure pathway and Z-scheme pathway. In the typical heterostructure pathway, the holes would migrate from the valence band of WO\textsubscript{3} to the HOMO levels of g-C\textsubscript{3}N\textsubscript{4}; the electrons in the LUMO levels of g-C\textsubscript{3}N\textsubscript{4} would combine with the electrons in the conduction band of WO\textsubscript{3}. In the Z-scheme pathway, the excited electrons in the conduction band of WO\textsubscript{3} can recombine with the holes in the HOMO levels of g-C\textsubscript{3}N\textsubscript{4} directly, leaving the electrons enriched in the LUMO levels of g-C\textsubscript{3}N\textsubscript{4}. As shown in Figure S5, the conduction band minimum of WO\textsubscript{3} (−0.37 eV, vs NHE) is less negative than the reduction potential of CO/CO\textsubscript{2} (−0.52 eV, vs NHE). As a result, the electrons in the conduction band of WO\textsubscript{3} cannot reduce the CO\textsubscript{2} molecules to produce CO effectively. Therefore, it is necessary for the photoinduced carriers to be separated in the Z-scheme pathway to reduce CO\textsubscript{2} into CO for WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4}. The generation of hydroxyl radicals *OH can be a strong and direct evidence to confirm that g-C\textsubscript{3}N\textsubscript{4}/WO\textsubscript{3} is a direct solid-state Z-scheme heterostructure.\textsuperscript{3,25} According to Figure S6, it can be confirmed that the charge carriers are separated in the Z-scheme way for WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} samples in this experiment.

The detailed improved photocatalytic mechanism of WO\textsubscript{3−x}/g-C\textsubscript{3}N\textsubscript{4}, illustrated in Figure 8, can be explained as follows. The photocatalytic reduction mechanism of CO\textsubscript{2} into CO can be explained by eqs 1−3:\textsuperscript{3,4−38}

\[\text{photocatalyst} + h\nu \rightarrow e^- + h^+ \]  
(1)

\[2\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+ + E_{\text{ox}} = +0.82 \text{ V vs NHE} \]  
(2)

\[2h^+ + \text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \]  
(3)

\[E_{\text{red}} = -0.52 \text{ V vs NHE} \]

To achieve efficient photoreduction of CO\textsubscript{2} into CO, the potential of electrons must be more negative than the reduction potential (\(E_{\text{red}} = -0.52 \text{ V vs NHE}\)) and the potential of holes must be more positive than the oxidation potential (\(E_{\text{ox}} = +0.82 \text{ V vs NHE}\)). Although the electrons and holes for g-C\textsubscript{3}N\textsubscript{4} can participate in the reaction directly, the photocatalytic activity is still limited because of the rapid recombination of charge carriers (Figure 5a). Both pure WO\textsubscript{3} and WO\textsubscript{3−x} nanorods exhibit a poor photocatalytic activity because of the relative low potential of conduction band minimum, as the photogenerated electrons can hardly participate in the reaction in eq 2. After WO\textsubscript{3−x} nanorods are composited with g-C\textsubscript{3}N\textsubscript{4} nanosheets, the holes in the HOMO levels of g-C\textsubscript{3}N\textsubscript{4} would combine with the electrons in the conduction band of WO\textsubscript{3−x}, separating the carriers efficiently in the Z-scheme pathway. As the LUMO levels of g-C\textsubscript{3}N\textsubscript{4} and the valence band maximum of WO\textsubscript{3} match the redox potential of CO\textsubscript{2} reduction (eqs 1−3), photogenerated carriers could react with the surface adsorbed CO\textsubscript{2} molecules to participate in the photoreduction reaction. It is noted that the photocatalytic activity can be further enhanced for WO\textsubscript{3−x}/g-C\textsubscript{3}N\textsubscript{4} samples by introducing the oxygen vacancies into the WO\textsubscript{3} surface. The energy levels of the oxygen vacancies locate at approximately 0.8 eV below the CBM of WO\textsubscript{3−x}. The electrons can be excited from the valence band to the energy levels of oxygen vacancies directly. The electrons in the conduction band of WO\textsubscript{3−x} would also be trapped by the energy levels of oxygen vacancies. As the energy levels of oxygen vacancies are close to the HOMO levels of g-C\textsubscript{3}N\textsubscript{4}, the electrons in the energy levels of oxygen vacancies can combine with holes in the HOMO levels of g-C\textsubscript{3}N\textsubscript{4} more easily, promoting the separation of photogenerated electrons and holes in the Z-scheme pathway. The holes left in the valence band of WO\textsubscript{3−x} can oxidize the H\textsubscript{2}O into H\textsuperscript{+} (eq 2), and the electrons left in the LUMO levels of g-C\textsubscript{3}N\textsubscript{4} can react with CO\textsubscript{2} and H\textsuperscript{+} to yield CO and H\textsubscript{2}O (eq 3). Therefore, the oxygen vacancies at the interface of WO\textsubscript{3−x} and g-C\textsubscript{3}N\textsubscript{4} could extend the visible-light response, facilitate the separation of charge carriers in the Z-scheme, and prolong the lifetime of electrons and holes, resulting in a significantly enhanced photocatalytic activity on the reduction of CO\textsubscript{2} into CO.

3. CONCLUSIONS

In summary, we have constructed oxygen vacancy-modified Z-scheme heterostructures by compositing WO\textsubscript{3−x} nanorods with g-C\textsubscript{3}N\textsubscript{4} nanosheets. The photocatalytic activity on the photoreduction of CO\textsubscript{2} into CO is remarkably enhanced for W\textsubscript{x}C\textsubscript{3} samples (WO\textsubscript{3−x} nanorods composited with 3 wt % of g-C\textsubscript{3}N\textsubscript{4}), compared to WO\textsubscript{3} g-C\textsubscript{3}N\textsubscript{4}, and WC\textsubscript{3} samples. It is revealed that the introduced oxygen vacancies result in defect energy levels below the conduction band of WO\textsubscript{3−x}, which extend the visible-light response, promote the separation of charge carriers in the Z-scheme, and prolong the lifetime of photogenerated electrons. This work may provide physical insights for designing and fabricating oxygen vacancy-modified novel heterostructures with highly efficient performance.

4. EXPERIMENTAL SECTION

4.1. Synthesis of WO\textsubscript{3−x}/g-C\textsubscript{3}N\textsubscript{4}. WO\textsubscript{3} nanorods were synthesized via the typical hydrothermal method: 3 mL of concentrated hydrochloric acid (12 mol/L) and 3.3 g of Na\textsubscript{2}WO\textsubscript{4}H\textsubscript{2}O were added into 70 mL of deionized water (18.2 M\textsubscript{Ω}cm) and a yellow floc formed immediately. This mixture was added with 20 g of K\textsubscript{2}SO\textsubscript{4} and then transferred into a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 24 h. After cooling down to room temperature, the obtained participates were washed with deionized water six times.
times and then dried at 60 °C for 10 h. The WO3 nanorods with oxygen vacancies were prepared by vacuum thermal treatment. WO3 powders (0.3 g) were placed in an electric vacuum drying oven. The vacuum pressure was 5–20 mTorr, and the temperature was elevated to 200 °C with a ramp rate of 10 °C/min. After vacuum thermal treatment for 5 h, the powders were placed in air and allowed to cool down to room temperature naturally and were labeled as WO3-vac. The g-C3N4 was prepared by directly calcining 20 g of urea in muffle with a heating rate of 2.5 °C min−1 and then kept at 550 °C for 3 h.

The WO3/g-C3N4 heterostructures were prepared as follows: WO3 powders (0.2 g) were dispersed into 50 mL of deionized water and ultrasonicated in 40 KHz for 3 h, which was designated as sample A. At the same time, g-C3N4 powders (6 mg) were dispersed in 50 mL of 0.02 mol/L hydrochloric acid and ultrasonicated in 40 KHz for 3 h, which was designated as sample B. Sample A was mixed with sample B under vigorous stirring for 12 h and dried in an oven for 10 h. The obtained powders were designated as WC3, where X% indicated the nominal weight ratio of g-C3N4 to WO3. Similarly, WO3/g-C3N4 was also prepared by the same procedure just by replacing the WO3-vac powders with the WO3 powders. The obtained samples were designated as WC3 (0.2 g of WO3 and 6 mg of g-C3N4).

4.2. Characterization. XRD patterns were collected on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Kα, λ = 1.54056 Å). HRTEM images were obtained by a JEOL 3010, for which the samples were prepared by applying a drop of ethanol suspension onto an amorphous carbon-coated copper grid and dried naturally. XPS measurements were carried out with a VG Scientific ESCA Lab 250i- XL spectrometer by using an unmonochromated Al Kα (1486.6 eV) X-ray source. All of the XPS images were calibrated with respect to the binding energy of the adventitious C 1s peak at 284.8 eV. Differences in the photoelectrochemical activities of the WO3/g-C3N4 heterojunctions were evaluated by cyclic voltammetry, as shown in Figure S1.

4.3. Evaluation of Photocatalytic Activity. The photocatalytic reduction of carbon dioxide (CO2) into carbon oxide (CO) was performed in a sealed 275 mL Pyrex glass reactor. Photocatalysts (100 mg) were uniformly dispersed on the round bottom of the reactor (about 18 cm2). This reactor was inflated with CO2 gas (99.999%) at a flow of 0.3 L/min for 45 min consistently to exclude other gases (for example, N2 and O2). Then, 0.4 mL of deionized water was injected into the reactor. The whole reactor was sealed and placed at 27 cm right below a 500W Xe lamp. At 2 h intervals, 0.4 mL of gas was extracted to detect the amount of yield CO by a gas chromatograph (GC 2010 plus, SHIMADZU).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01969.

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