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## Synthesis of $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ for enhanced photocatalytic $\text{CO}_2$ reduction with a Z-scheme mechanism†

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$\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  nanoscale composites with a Z-scheme mechanism were successfully synthesized by high temperature calcination combined with a hydrothermal method. These synthesized composites exhibited excellent photocatalytic performance, especially the 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite, which produced about 1.8 times the CO yield of pure  $\text{g-C}_3\text{N}_4$ . The obtained products were characterized by X-ray diffraction (XRD) patterns, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and so on. Characterization results revealed that Bi ions had well covered the surface of  $\text{g-C}_3\text{N}_4$ , thus restraining the recombination of electron–hole pairs and resulting in a stronger visible-light response and higher CO yield. In addition, the electron transfer process through the Z-scheme mechanism also promoted the photocatalytic activity.

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## 1. Introduction

In recent years, the continuous development of industry and the serious destruction of forest vegetation have led to difficulties in controlling  $\text{CO}_2$  emission, thus seriously threatening the survival and development of mankind.<sup>1–6</sup> Recently, the field of  $\text{CO}_2$  photocatalytic reduction which translates  $\text{CO}_2$  into some useful substances has attracted many research teams.<sup>7–12</sup> As we all know, many narrow band gap semiconductor based photocatalysts have been used in  $\text{CO}_2$  photocatalytic reduction.<sup>13–15</sup> Among them,  $\text{g-C}_3\text{N}_4$  is the most widely used one due to its suitable band gap, simple and convenient preparation and good visible light response.<sup>16,17</sup> However, there are still many obvious shortcomings associated with this catalyst, such as its small range of light response, low separation rate of electron–hole pairs and unsatisfactory performance in the photocatalytic reaction. Lots of methods have been developed to improve the photocatalytic performance of  $\text{g-C}_3\text{N}_4$ , such as element modification,<sup>18–20</sup> texture fabrication<sup>21,22</sup> and heterojunction formation.<sup>23–27</sup> Fabrication of a heterojunction between two semiconductors is a promising way among these methods, in

which the formation of an internal electric field and the promoted separation of charge carriers effectively restrains the recombination rate of electron–hole pairs.<sup>28</sup>

As an important semiconductor material,  $\text{Bi}_2\text{O}_3$  has been applied in many fields like electronic ceramics, optoelectronic devices, high-temperature superconductors, catalysts, and sensors due to its special physical properties and crystal structure.<sup>29–33</sup> What's more,  $\text{Bi}_2\text{O}_3$  also has been used as a normal photocatalyst in water splitting and photodegradation pollutant. Unfortunately, its photoreduction performance is poor owing to the low migration of photo-charges, which leads to a fast combination of photogenerated electron–hole pairs.<sup>34–37</sup> For the improvement of photocatalytic ability over  $\text{Bi}_2\text{O}_3$ , the construction of heterojunction is considered as an effective measure to reduce the probability of electron–hole pairs recombination, like  $\text{BiOCl}/\text{Bi}_2\text{O}_3$ ,<sup>38</sup>  $\text{BiVO}_4/\text{Bi}_2\text{O}_3$  (ref. 39) and  $\text{Bi}_2\text{O}_3/\text{TiO}_2$ .<sup>40</sup> It is known that an internal electric field is produced after the formation of a p–n heterojunction. The photocarriers are greatly accelerated by the electric field, which effectively suppresses the reflux of photogenerated carriers and thus improves the photocatalytic performance.<sup>41</sup> Due to the presence of heterojunctions, the excitation wavelength of light is also extended at the same time.<sup>42</sup>

From the above analysis, it can be presumed that there exists a possibility to construct a heterostructure between  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  through their mutual activation. However, the use of  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  heterojunctions for  $\text{CO}_2$  photoreduction has not been reported. Therefore,  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  compounds with different  $\text{Bi}_2\text{O}_3$  contents were prepared and used in  $\text{CO}_2$  photocatalytic reduction in this study. It was found that the yields of  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  compounds was higher than single  $\text{Bi}_2\text{O}_3$  or  $\text{g-C}_3\text{N}_4$ .

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$\text{C}_3\text{N}_4$ . Moreover, the visible light response is also enhanced. Based on the results of all the characterization techniques, the possible promotion mechanism is also raised.

## 2. Experimental

### 2.1. Chemicals

Urea ( $\text{H}_2\text{NCONH}_3$ ) and bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) were purchased from Sinopharm Chemical Reagent Corp, P. R. China. All of these purchased reagents are of analytical grade and used directly.

### 2.2. Synthesis

Pure  $\text{g-C}_3\text{N}_4$  was obtained by heating urea in air at  $550^\circ\text{C}$  for 2 h. The  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composites with different  $\text{Bi}_2\text{O}_3$  mass ratio (0, 20, 40, 60 and 80 wt%) were gained through the following procedure:  $\text{g-C}_3\text{N}_4$  (0.5 g) was dissolved in 60 mL of ethylene glycol and sonicated for 30 min to yield the  $\text{g-C}_3\text{N}_4$  sheet. Subsequently, a certain amount (0.104, 0.208, 0.312, 0.416 g) of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and urea (1 g) were added in the solution and stirred for 1 h. The solution was then transferred to Teflon-lined autoclave (100 mL) and hydrothermally treated at  $180^\circ\text{C}$  for 12 h. The obtained product was rinsed several times with deionized water and dried overnight at  $80^\circ\text{C}$ . The hydrothermal product was then calcined in air at  $380^\circ\text{C}$  for 2 h to get the final product. Pure  $\text{Bi}_2\text{O}_3$  was obtained by the same procedure without the adjunction of  $\text{g-C}_3\text{N}_4$ .

### 2.3. Characterization

The crystal phase of catalyst was determined by X-ray diffraction (XRD, Bruker D8, Cu  $\text{K}\alpha$  radiation), and the morphology of the synthesized samples were investigated by scanning electron microscope (SEM, Phillips XL-30 FEG/NEW) and transmission electron microscope (TEM, Phillips Model CM200). The chemical elements of the compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250xi, USA) and Al  $\text{K}\alpha$  radiation sources. The Brunauer–Emmett–Teller (BET, Quantachrome Autosorb-iQ-AG instrument) pore structure and surface area were measured by  $\text{N}_2$  adsorption–desorption at  $-196^\circ\text{C}$ . UV-vis diffuse reflectance spectrum was analyzed in the range of 250–800 nm on a spectrophotometer (SHIMADZU UV-3600, Japan) using  $\text{BaSO}_4$  as the reflectance standard material. Photoluminescence (PL) was measured by a fluorescence spectrophotometer (Hitachi F-4600, 325 nm excitation wavelength).

### 2.4. Photoelectrochemical

Photoelectrochemical included electrochemical impedance spectroscopy (EIS) and transient photocurrent responses analysis were carried out on an electrochemical instrument (CHI 660E). A standard three-electrode system was immersed in a  $\text{Na}_2\text{SO}_4$  electrolyte solution (0.5 M). The Pt and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. FTO conductive glass covered by the synthesized sample was used as working electrode, and it was gained by the following method: mixture solution was consisted of Nafion (20

$\mu\text{L}$ , 5%) and ethanol (1 mL). After that, 10 mg of the synthesized sample was dropped into the mixed solution and ultrasonically dispersed (2 h), then drop the slurry (0.1 mL) on  $1 \times 1\text{ cm}$  FTO glass. Therefore, the sample was well attached to the surface of the glass piece after evaporation of the ethanol. In addition, photocurrent and EIS measurements were performed under the illumination of the simulated solar light.

### 2.5. Photoactivity

The  $\text{CO}_2$  photoreduction experiment was performed with a reactor (500 mL) in a gas-enclosed circulation system. During the reaction, a Xenon lamp (300 W) was used as the light source. The experimental procedure was designed as follows: 50 mg sample was dispersed in 100 mL deionized water, then magnetic stirring was performed at an appropriate rotation speed. The reactor was vacuum treated and 100 kPa of high purity  $\text{CO}_2$  was passed into the reactor under the throttling of airflow. Then this pressure was kept for 30 min to obtain the balance of adsorption–desorption. Throughout the experiment, the temperature was maintained at  $25^\circ\text{C}$ . The gas (0.15 mL) in reactor was obtained and analyzed by a gas chromatography (GC-2010 Plus, SHIMADZU, Japan) in the course of the reaction.

## 3. Results and discussion

### 3.1. SEM, XRD and TEM

The SEM patterns of  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composites are exhibited in Fig. 1. Clearly, the  $\text{g-C}_3\text{N}_4$  exhibits a curled layered structure (Fig. 1a), and the  $\text{Bi}_2\text{O}_3$  shows a distinct rod-like structure (Fig. 1b). Fig. 1c shows the SEM image of 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  sample and its corresponding elemental mapping images. It could be observed from Fig. 1c that 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite perfectly retains the form of  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$ , showing a curled sheet structure. In addition, the mapping images of 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite in Fig. 1c also reveals the coexistence of C, N, O and Bi elements.

The XRD patterns of all composites are displayed in Fig. 2. In the pattern of  $\text{g-C}_3\text{N}_4$ , the diffraction peak observed at  $27.3^\circ$  could be attributed to the (002) plane of  $\text{g-C}_3\text{N}_4$  (JCPDS 87-1526). The peak at  $12.7^\circ$  is the (100) plane of  $\text{g-C}_3\text{N}_4$ , corresponding to the in-plane structure packing motif of tri-*s*-triazine units.<sup>43</sup> The synthesized  $\text{Bi}_2\text{O}_3$  represents six major peaks at  $2\theta = 27.8^\circ$ ,  $31.7^\circ$ ,  $32.6^\circ$ ,  $46.2^\circ$ ,  $55.4^\circ$  and  $74.4^\circ$ , corresponding to the (201), (002), (220), (222), (421) and (423) planes respectively, which is in consistent with the  $\beta\text{-Bi}_2\text{O}_3$  (JCPDS 65-1209). As the content of  $\text{Bi}_2\text{O}_3$  in  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  samples increase, the intensity of  $\text{g-C}_3\text{N}_4$  peak becomes weaker. As a contrast, the peak intensity of  $\text{Bi}_2\text{O}_3$  becomes stronger, especially for the diffraction peak at  $27.8^\circ$ , revealing the increased crystallinity of  $\text{Bi}_2\text{O}_3$ .

The TEM images of samples are demonstrated in Fig. 3. Fig. 3a and b reveal the microscale morphology of  $\text{g-C}_3\text{N}_4$  and  $\text{Bi}_2\text{O}_3$ , which are characterized by a curled edge and a rod-like structure respectively, as also revealed by the SEM patterns. The TEM pattern of 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite shows that  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  are combined together uniformly (Fig. 3c). In addition, the 0.318 nm interplanar spacing corresponding to



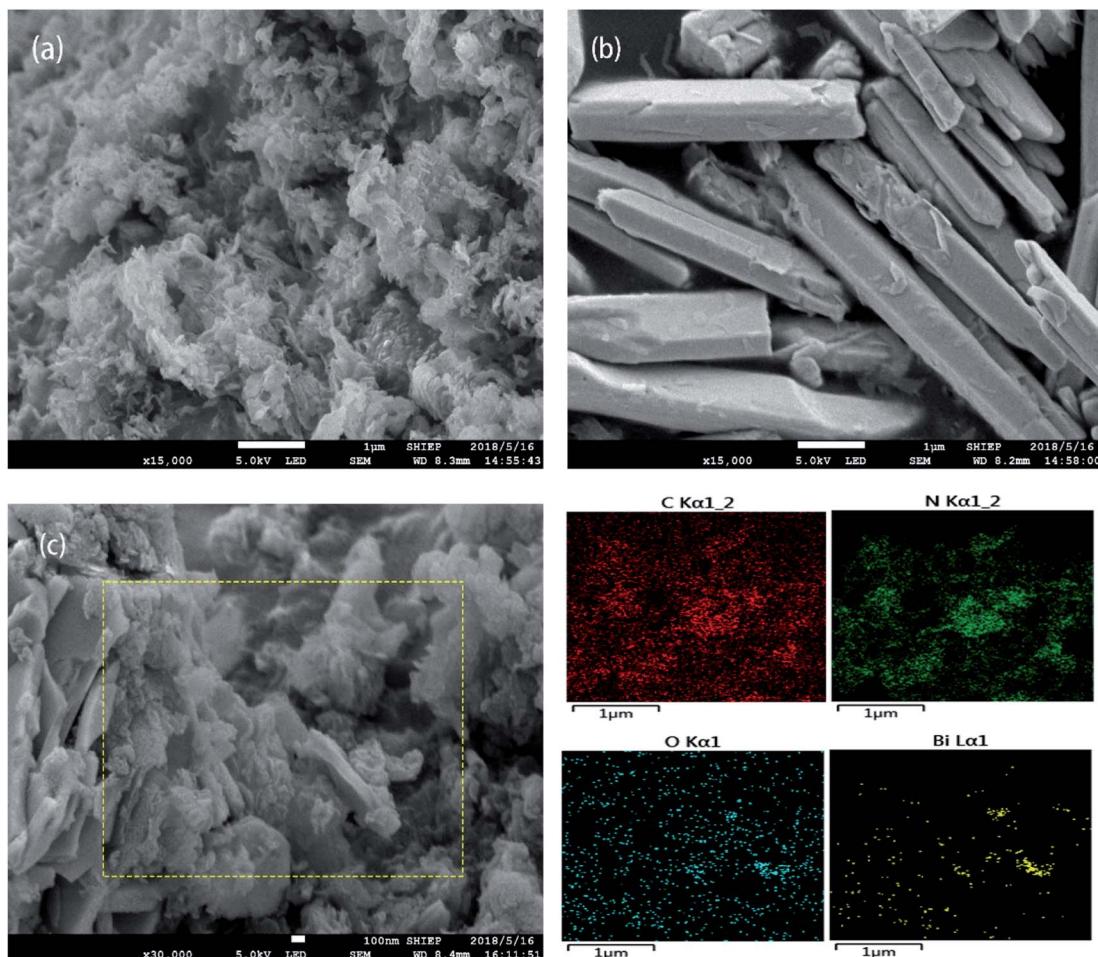


Fig. 1 SEM of  $\text{g-C}_3\text{N}_4$  (a) and  $\text{Bi}_2\text{O}_3$  (b); SEM and elemental mapping of C, N, O and Bi in 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite (c).

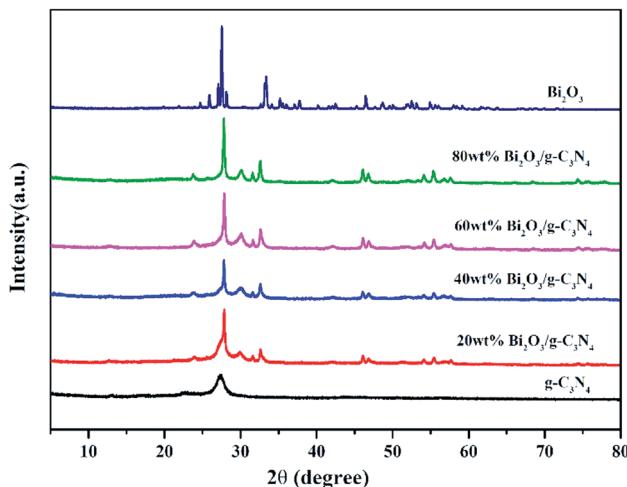


Fig. 2 XRD of  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composites.

the (201) crystal plane of the cubic  $\text{Bi}_2\text{O}_3$  is visible in the high resolution TEM image (Fig. 3d).<sup>44</sup> The results show that  $\text{g-C}_3\text{N}_4$  and the rod-like  $\text{Bi}_2\text{O}_3$  have deeply combined together in 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite.

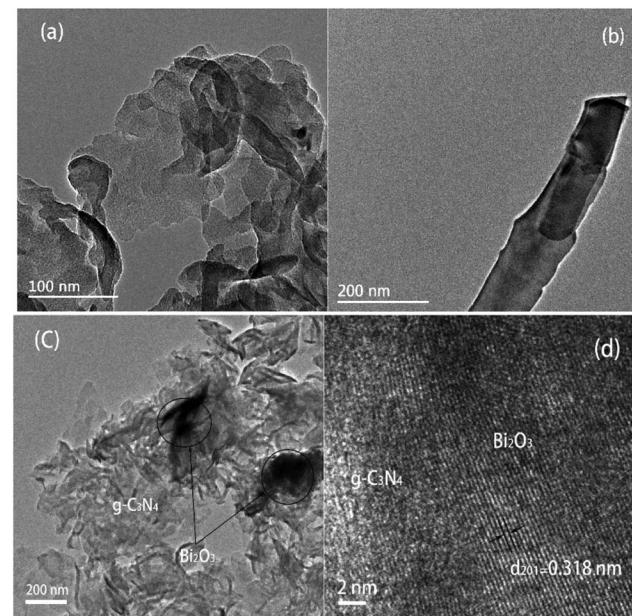


Fig. 3 TEM image of  $\text{g-C}_3\text{N}_4$  (a),  $\text{Bi}_2\text{O}_3$  (b) and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  (c); HRTEM of 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  (d).

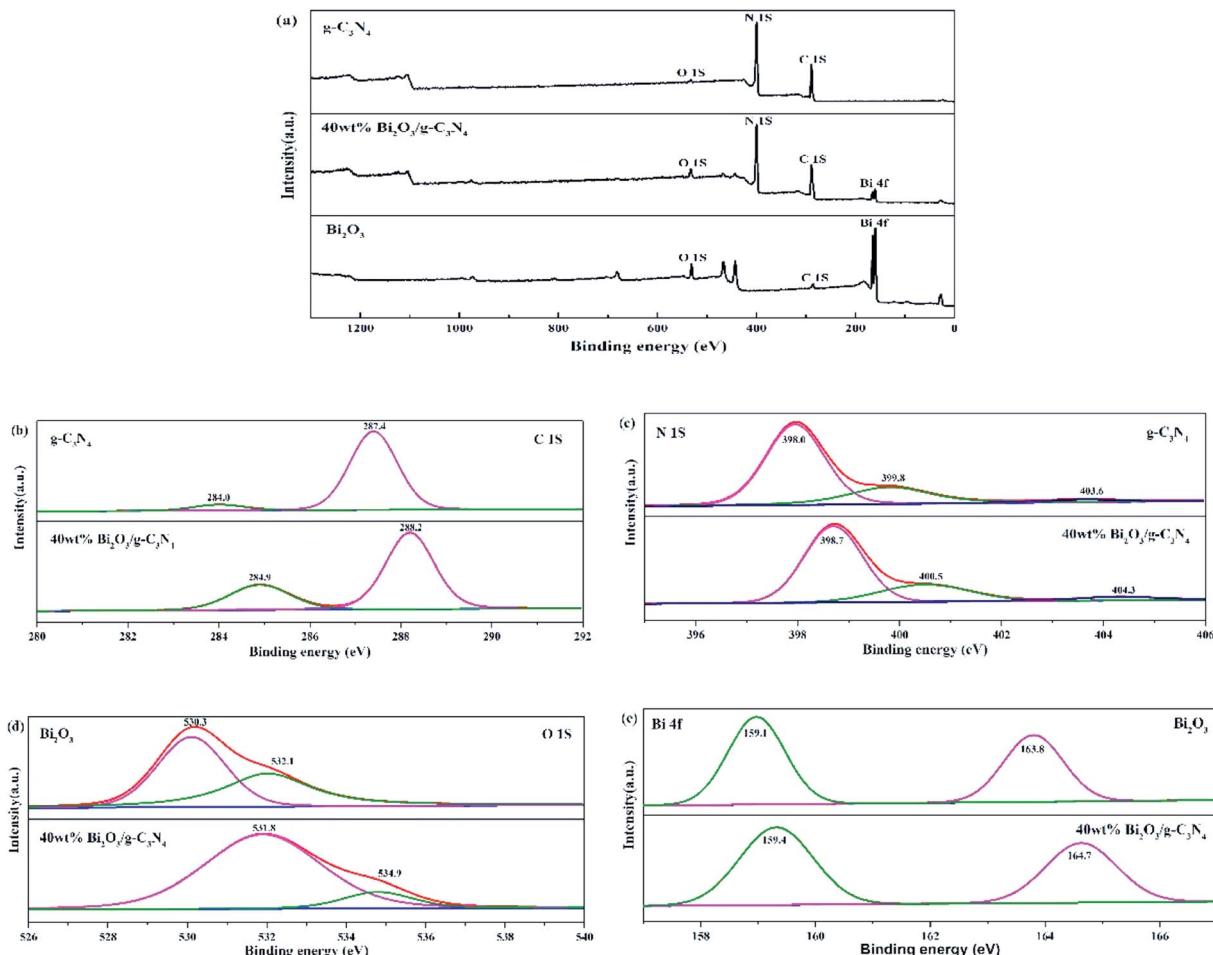


Fig. 4 XPS of  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  (a); high-resolution C 1s (b) and N 1s (c) of  $\text{g-C}_3\text{N}_4$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ ; high-resolution O 1s (d) and Bi 2p (e) of  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ .

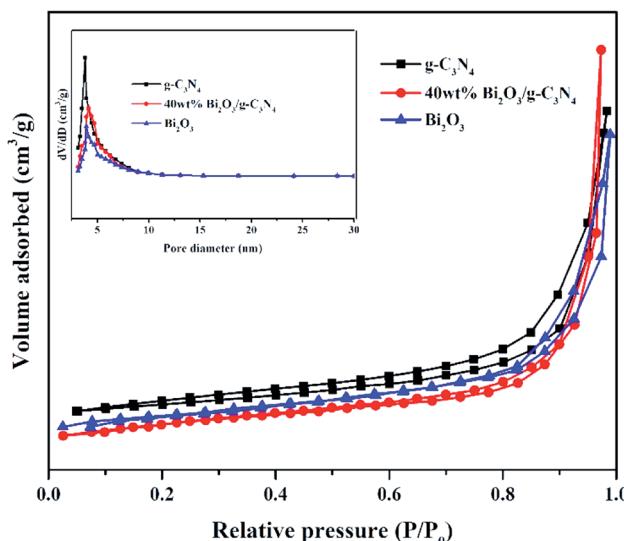


Fig. 5  $\text{N}_2$  adsorption–desorption isotherms and pore size distribution curves (inset) of  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite.

Table 1 Textural properties of  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composites

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	Pore size (nm)
$\text{g-C}_3\text{N}_4$	66.7	3.839
20 wt% $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$	109.2	3.834
40 wt% $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$	136.1	3.821
60 wt% $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$	98.3	3.849
80 wt% $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$	78.2	3.815
$\text{Bi}_2\text{O}_3$	53.2	3.856

### 3.2. XPS, BET and UV

The compositions of chemical elements on  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  were analyzed by XPS. As the XPS spectra show (Fig. 4a), C 1s and N 1s signals are available in  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ , while Bi 4f and O 1s peaks are detected in  $\text{Bi}_2\text{O}_3$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  respectively, which means that  $\text{Bi}_2\text{O}_3$  is successfully doped into  $\text{g-C}_3\text{N}_4$ . Carbon contained in  $\text{Bi}_2\text{O}_3$  sample might be caused by extraneous carbon. The corresponding detailed spectra of C 1s, N 1s, O 1s

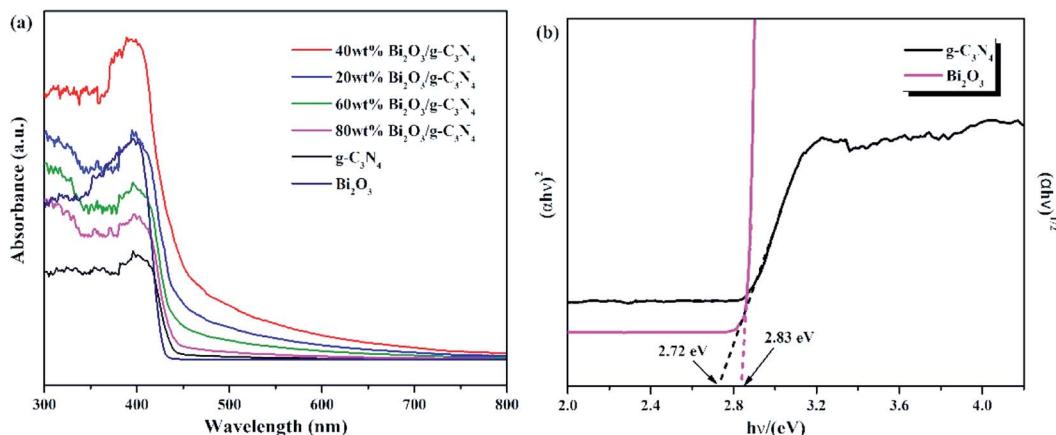


Fig. 6 (a) UV-vis DRS for g-C<sub>3</sub>N<sub>4</sub>, Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites. (b)  $(\alpha h\nu)^{1/2}$  and  $(\alpha h\nu)^2$  versus energy ( $h\nu$ ) for the band gap energies of g-C<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>O<sub>3</sub>, respectively.

and Bi 4f are also exhibited in Fig. 4. In the C 1s spectrum of g-C<sub>3</sub>N<sub>4</sub>, two sub-bands centered at 287.4 and 284.0 eV could be observed (Fig. 4b), corresponding to the N-C=N group and the C-C bond, respectively.<sup>45</sup> Fig. 4c exhibits the N 1s spectra of g-C<sub>3</sub>N<sub>4</sub> and 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. The dominant peak at 398.0 eV could be considered as the carbon-bonded sp<sup>2</sup>-hybrid aromatic N (C=N-C),<sup>46</sup> while the other two peaks located at 399.8 eV and 403.6 eV could be attributed to the tertiary nitrogen N-(C)<sub>3</sub> groups and  $\pi$  excitations.<sup>47</sup> The high-resolution O 1s spectrum of Bi<sub>2</sub>O<sub>3</sub> is shown in Fig. 4d, in which the protruding peaks at 530.3 eV and 532.1 eV are derived from the Bi-O bond. Two peaks are observed in high-resolution Bi 4f spectrum of Bi<sub>2</sub>O<sub>3</sub> (Fig. 4e): the peak of Bi 4f at 159.1 eV and 163.8 eV reveal the presence of Bi<sup>3+</sup> in Bi<sub>2</sub>O<sub>3</sub>.<sup>48,49</sup> The band energy shift of most peaks could be found in the spectrum of the 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. The shift should be originated from the different electron concentrations,<sup>50</sup> which are corresponding to the SEM, XRD and TEM results mentioned above.

Nitrogen adsorption-desorption measurements were performed at  $-196^{\circ}\text{C}$  to analyze the textural features of the Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite. All samples show

a type IV isotherm with a hysteresis loop (Fig. 5), revealing the presence of mesoporous structure into the composite. The specific surface area and average pore size of photocatalysts are listed in Table 1. Obviously, 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite possesses the largest specific surface area ( $136.1\text{ m}^2\text{ g}^{-1}$ ), while that for g-C<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>O<sub>3</sub> are  $66.7\text{ m}^2\text{ g}^{-1}$  and  $53.2\text{ m}^2\text{ g}^{-1}$  respectively. Correspondingly, more active sites are available on 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite. The BJH pore size distribution of g-C<sub>3</sub>N<sub>4</sub>, Bi<sub>2</sub>O<sub>3</sub> and 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> is shown in the inset of Fig. 5. Obviously, all the three samples exhibit a fairly narrow and limited pore size distribution between 3.6–4.1 nm.

The optical properties of Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites were tested by UV-vis measurement, and the relevant data were converted from the Kubelka-Munk equation. The 450 nm absorption edge of g-C<sub>3</sub>N<sub>4</sub> could be observed in Fig. 6a, while the Bi<sub>2</sub>O<sub>3</sub> shows a similar absorption properties. It can be found that Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> samples could obtain more photons during the reaction according to the vertical coordinates, which is good to the photoreduction of CO<sub>2</sub>. The band gap energy of Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> could be figured out by the formula:  $\alpha h\nu = A (h\nu - E_g)^{n/2}$ , where  $\alpha$ ,  $h$ ,  $\nu$ ,  $A$  and  $E_g$  are the

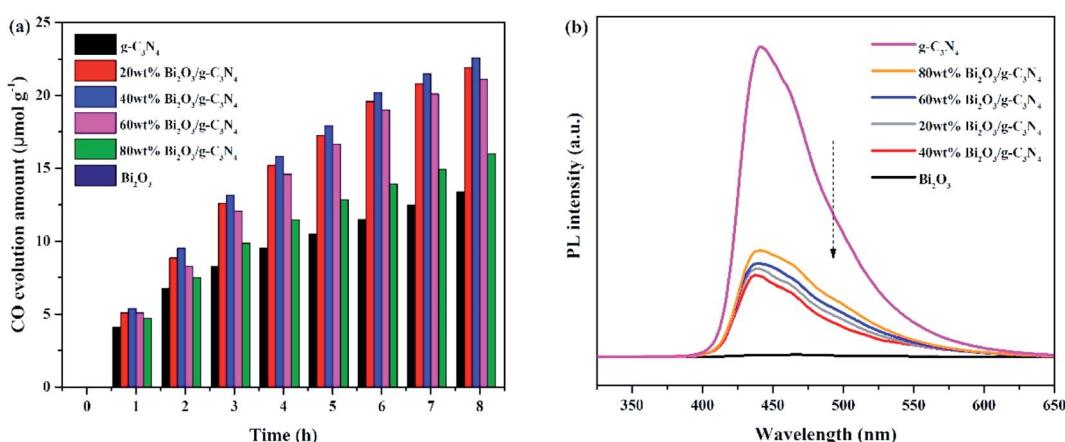


Fig. 7 (a) Yield of CO and (b) PL spectra of all samples.



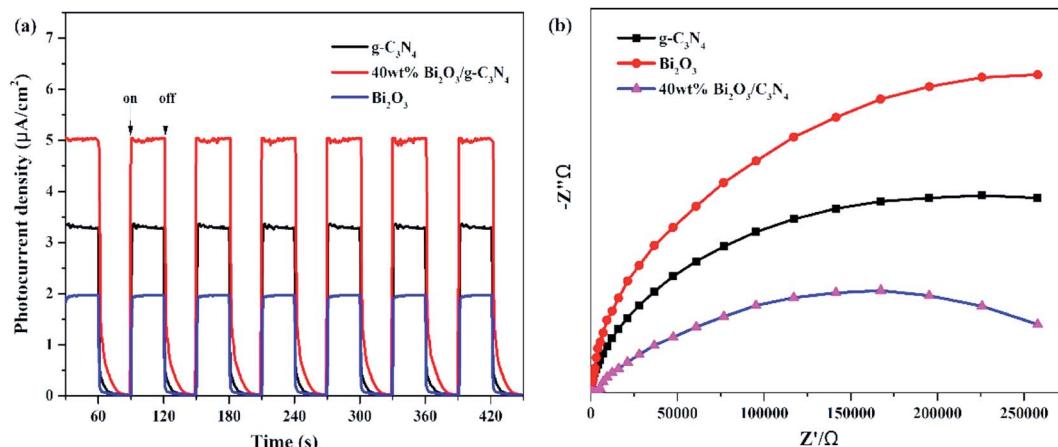


Fig. 8 (a) Transient photocurrent density and (b) electrochemical impedance spectra of  $\text{Bi}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite.

absorption coefficient, Planck constant, light frequency, band gap energy and constant related to the catalyst. Among them,  $n$  relies on optical transition type of the semiconductor ( $n = 4$  for indirect transition and  $n = 1$  for direct transition). For  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$ , the values of  $n$  are 1 and 4, respectively.<sup>51-53</sup> According to Fig. 6b, the  $E_g$  values of  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  are counted to be 2.83 and 2.72 eV respectively.

### 3.3. Photocatalytic activity, PL and photoelectrochemical

The photocatalytic activities of all samples are tested and CO was found as the main product. In addition, the control experiments were also conducted. No hydrocarbon products are tested without simulated solar light or sample, revealing that the conditions mentioned above are essential for the  $\text{CO}_2$  photocatalytic reduction. Fig. 7a demonstrated the amount of CO production over the photocatalysts during the light irradiation. It could be clearly seen that the pure  $\text{Bi}_2\text{O}_3$  sample has not produced any CO, which means that pure  $\text{Bi}_2\text{O}_3$  cannot reduce  $\text{CO}_2$  to CO under photocatalytic conditions, due to the fact that the CB edge of  $\text{Bi}_2\text{O}_3$  is lower than the reduction potential of  $\text{CO}_2/\text{CO}$  (−0.52 V vs. NHE).<sup>54</sup> The yield of  $\text{g-C}_3\text{N}_4$  is also not high, indicating that the photocatalytic performance of pure catalyst is not very well, which can be ascribed to the fast recombination

Table 2 The production rate of redox products for  $\text{g-C}_3\text{N}_4$  and 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$

Sample	Reduction products ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )			Oxidation products ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Ratio $e^- : h^+$
	CO	$\text{CH}_4$	$\text{H}_2$	$\text{O}_2$	
$\text{g-C}_3\text{N}_4$	1.68	0.38	1.11	2.42	0.89 : 1
40 wt% $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$	2.81	1.34	1.38	6.95	0.88 : 1

rate of electron–hole pairs in reaction. A great enhancement of CO yield is detected in terms of the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composites. Moreover, the photocatalytic activity enhances as the increasing  $\text{Bi}_2\text{O}_3$  content in the composites, which is owing to the increased quantity of the heterojunctions. During the reaction, the highest CO yield ( $22.5 \mu\text{mol g}^{-1}$ ) is achieved on 40 wt%  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ , which is about 1.8 times the CO yield of  $\text{g-C}_3\text{N}_4$ . However, the photocatalytic performance would decline along with the excessive addition of  $\text{Bi}_2\text{O}_3$ , which might be aroused by the reduce of the specific surface area, and the excessive  $\text{Bi}_2\text{O}_3$  might act as the recombination core of electron–hole pairs

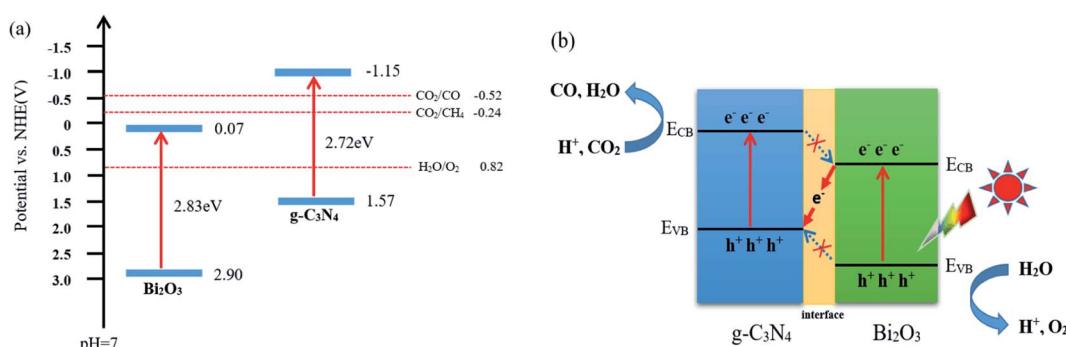


Fig. 9 (a) Band gap energy and band positions of  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  together with  $\text{CO}_2/\text{CO}$ ,  $\text{CO}_2/\text{CH}_4$  and  $\text{H}_2\text{O}/\text{O}_2$  redox potentials at pH = 7 and (b) Z-type mechanism of  $\text{CO}_2$  photoreduction route on  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  composite.



during the reaction.<sup>55,56</sup> The photocatalytic stability of all composites and g-C<sub>3</sub>N<sub>4</sub> are shown in the Fig. S1,† the yield of CO keeps stable during three experimental runs, revealing that the performance of all composites and g-C<sub>3</sub>N<sub>4</sub> are stable during the reaction. To further probe the truth, the separation efficiency was characterized by PL. As shown in Fig. 7b, the emission peak of Bi<sub>2</sub>O<sub>3</sub> is almost invisible in the 450–500 nm range, which may be due to a trace of surface defects or surface oxygen vacancies of Bi<sub>2</sub>O<sub>3</sub>. Compared with Bi<sub>2</sub>O<sub>3</sub>, a strong peak concentrated at 450 nm could be noticed in the g-C<sub>3</sub>N<sub>4</sub> spectrum, which reflects the fast recombination rate of electrons–hole pairs.<sup>57</sup> Different from g-C<sub>3</sub>N<sub>4</sub>, the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites exhibit a moderate peak intensity in the pattern, suggesting that heterojunctions are built among Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, so the holes and electrons are effectively separated. Therefore, the recombination rate is greatly reduced, which is good to enhance the activity of CO<sub>2</sub> photoreduction. In addition, the 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> has the lowest peak intensity among all the synthesized Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> samples.

In addition to PL measurements, photo-electrochemical measurements are used to further analyze the properties of photoelectrons in Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. Fig. 8a shows the photocurrent response of the samples under visible light absorption. Transient photocurrent measurements could show more evidence for the rapid electron transfer efficiency in the photocatalyst. In the light-on and light-off tests, all the photocatalysts show rapid and intense photocurrent response, indicating that the photocatalytic activity is relatively stable. Both Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> exhibit a rapidly increasing current when light is on and an abruptly decreasing signal when the light is off. This transient response behavior might be resulted from the capture and release of electrons caused by surface defects.<sup>58</sup> In addition, the photocurrent intensity of 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructured composite is 2.5 and 1.5 times the intensity of Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, respectively, indicating that 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> has higher charge separation efficiency and better photocatalytic properties than pure catalysts. To confirm this inference, the EIS experiment was also performed. The semicircular Nyquist plots of the samples are presented in Fig. 8b. Obviously, a smaller semicircle diameter could be detected on the plot of 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> than that of pure Bi<sub>2</sub>O<sub>3</sub> and pure g-C<sub>3</sub>N<sub>4</sub>, indicating that the electron transfer rate is faster in 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>,<sup>59</sup> which is corresponding to the previous photocatalytic activity results.

### 3.4. Mechanism

According to the characterization and CO<sub>2</sub> photocatalytic reduction test results of the prepared samples, the reaction mechanism of CO<sub>2</sub> reduction over Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites were proposed. As shown in Fig. 9a, the valence band (VB) and conduction band (CB) of a semiconductor could be determined using the following equation:<sup>60</sup>  $E_{CB}^0 = \chi - E^C - 1/2E_g$ . Where  $\chi$  is the absolute electronegativity of the semiconductor ( $\chi$  for Bi<sub>2</sub>O<sub>3</sub> is 5.986 eV),  $E^C$  is the energy of free electrons in the hydrogen size (4.5 eV) and  $E_g$  is the band gap of the semiconductor.<sup>61,62</sup> Combined with the results in Fig. 6b, the conduction band (CB)

and valence band (VB) values for the pure Bi<sub>2</sub>O<sub>3</sub> are 0.07 eV and 2.90 eV, respectively. For g-C<sub>3</sub>N<sub>4</sub>, the VB is −1.57 eV, and the CB is 1.15 eV.<sup>63,64</sup> The charge transfer in the interface can follow a double-transfer mode or a Z-scheme transfer mechanism. Double-transfer means that the CO<sub>2</sub> reduction reaction would happen on the CB of Bi<sub>2</sub>O<sub>3</sub>, and the H<sub>2</sub>O oxidation reaction would occur on the VB of g-C<sub>3</sub>N<sub>4</sub>. In fact, the CB of Bi<sub>2</sub>O<sub>3</sub> is lower than the reduction potential level of CO<sub>2</sub>/CO (−0.52 V vs. NHE), thus the reduction of CO<sub>2</sub> would not proceed and CO would not be generated, which means that double-transfer mechanism is not suitable here to explain. Z-scheme transfer mechanism is different from the double-transfer mechanism, as shown in Fig. 9b, the photo-induced electrons on the surface of Bi<sub>2</sub>O<sub>3</sub> can easily be transferred to g-C<sub>3</sub>N<sub>4</sub> through the interface, the holes on VB of Bi<sub>2</sub>O<sub>3</sub> are captured by H<sub>2</sub>O molecules to produce O<sub>2</sub> and protons. At the same time, the CO<sub>2</sub> molecules react with the electrons on the CB of g-C<sub>3</sub>N<sub>4</sub> to generate CO and H<sub>2</sub>O with the participation of protons. Moreover, the formation of other products including CH<sub>4</sub>, H<sub>2</sub>, and O<sub>2</sub> were also observed in the experimental process, and the charge balance table is shown in Table 2. The enhanced activity of 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> in CO<sub>2</sub> reduction is mainly due to the Z-scheme heterostructure, which effectively delays the rapid recombination of the electron–hole pairs in Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, therefore improving the photocatalytic activity.

## 4. Conclusions

In general, Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanoscale composites with heterojunction was successfully synthesized by the combination of high temperature calcination and hydrothermal method. The 40 wt% Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite has the highest CO yield in the CO<sub>2</sub> photocatalytic reduction, which is 1.8 times the yield of that g-C<sub>3</sub>N<sub>4</sub>. This obvious improvement in photoactivity is mainly due to the effective separation of electron–hole pairs and successive charge transfer through the interface. Moreover, the enhancement of specific surface area and visible light response also upgrade the photocatalytic performance of Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite. This study gives some valuable opinion for the research of g-C<sub>3</sub>N<sub>4</sub>-related photocatalysts.

## Conflicts of interest

There are no conflicts to declare.

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