Facile structure design based on C₃N₄ for mediator-free Z-scheme water splitting under visible light†

Guixia Zhao,‡ Xiubing Huang,‡ Federica Fina, Guan Zhang and John T. S. Irvine*

In this work, two photocatalysts (i.e., C₃N₄ and WO₃) were successfully combined into a heterojunction structure by a facile hydrothermal method for mediator-free overall water splitting, analogous to the natural photosynthesis over a two-step photoexcitation Z-scheme system. Hydrogen and oxygen are evolved with a 2:1 ratio by irradiating the C₃N₄-WO₃ composites loaded with Pt under visible light (λ > 420 nm) without any redox mediator. Introducing reduced graphene oxide (rGO) into the C₃N₄-WO₃ composites enhances the water splitting efficiency. Through optimizing the mass ratio in the C₃N₄-WO₃ composites, rGO content, amount of loaded Pt and pH value of the reacting system, the highest H₂/O₂ evolution rates of 2.84 and 1.46 μmol h⁻¹ can be obtained, with a quantum yield of 0.9%. Our findings demonstrate that the hydrothermal method is a promising strategy for constructing intimate heterostructures for Z-scheme water-splitting systems without using any redox mediator, and that rGO can be used to further enhance the performance in optimized conditions.

1. Introduction

With the increasing energy demand and concerns about environmental issues, hydrogen gas is considered as a promising fuel because it produces no carbon emission and other harmful by-products. The artificial photosynthesis for hydrogen generation through water splitting under visible light is an important approach, among which, the powdered-type two-step photoexcitation system, i.e., Z-scheme photocatalysis system, is the most similar to natural photosynthesis. Normally, a Z-scheme system contains two photocatalysts (one for H₂ evolution, and the other for O₂ evolution) and usually an electron mediator, which transfers the electrons from the excited O₂ photocatalyst to the holes generated in the H₂ photocatalyst. It is suggested that electron transfer is the rate-determining process. The commonly used electron mediators are ionic redox couples such as IO₃⁻/I⁻ or Fe³⁺/Fe²⁺. Compared with these ionic redox couples, the solid electron shuttle is more advanced for the recycle of the photocatalyst and cleaning of water. The challenges for the efficient H₂/O₂ evolution lie in the electron-accepting and donating abilities of the mediator, which should retain a dynamic equilibrium and remain stable during reactions. Furthermore, interface contact in the ternary system also plays an important role in maintaining continuous electron flow between the two photocatalysts. Considering the extremely high conductivity and specific surface area of graphene, it may be a good candidate as electron mediator for a Z-scheme system. Besides, it is also challenging to choose appropriate photocatalysts for realizing the intimate physical interaction with graphene, the efficient charge carrier separation, the H₂/O₂ evolution on the H₂/O₂ photocatalysts and then finally preventing water formation due to the backward reaction of H₂ and O₂. In Iwase et al.’s report, it has been shown that photoreduced graphene oxide (PRGO) was able to function as a solid electron mediator for Z-scheme overall water splitting, where SrTiO₃:Rh or BiVO₄ was used as O₂ evolution photocatalyst, and 0.7 wt% Ru as co-catalyst, and BiVO₄ was used as O₂ evolution photocatalyst. The PRGO was synthesized by photoreduction, i.e., irradiating the mixture of graphene oxide and the photocatalyst (Ru/SrTiO₃:Rh or BiVO₄) in the presence of methanol as electron donor. For the combined PRGO/BiVO₄ and Ru/SrTiO₃:Rh under pH 3.5, the H₂ evolution rate is ca. 8 μmol h⁻¹, while under neutral conditions, the performance is much lower, which is considered to be due to the poor physical interaction between PRGO/BiVO₄ and Ru/SrTiO₃:Rh under neutral conditions. In total, the reported Z-scheme based on PRGO is complicated in preparation as the noble metals (i.e., Ru and Rh) are used as co-catalyst and dopant, respectively, and the
performance is dependent on the acidity. Although Sasaki et al.\textsuperscript{a,6} reported the interparticle electron transfer without any electron mediator, the water splitting can only proceed efficiently by acidifying the aqueous solution to realize the effective contact through the aggregation of the two photocatalysts, Ru/SrTiO\textsubscript{3}-Rh and BiVO\textsubscript{4}. Thus, more sturdy contacts between the H\textsubscript{2}/O\textsubscript{2} evolution photocatalysts need to be found.

Since the introduction of graphitic carbon nitride (C\textsubscript{3}N\textsubscript{4}) into heterogeneous catalysis in 2006,\textsuperscript{1,14,15} this yellow polymer consisting of tri-s-triazines interconnected via tertiary amines has attracted increasing interest in materials research especially in H\textsubscript{2}-evolution photocatalysis under visible light.\textsuperscript{16-18} The band gap of C\textsubscript{3}N\textsubscript{4} is ca. 2.7 eV, with the CB and VB positions located at ca. −1.1 eV and ca. +1.6 eV vs. normal hydrogen electrode (NHE), respectively.\textsuperscript{16,19} More importantly, the preparation of C\textsubscript{3}N\textsubscript{4} is low cost since it only consists of two elements (C and N). For O\textsubscript{2}-evolution photocatalysis from water, tungsten trioxide (WO\textsubscript{3}) has been widely investigated because of its suitable bandgap, high electron mobility, abundance and low cost.\textsuperscript{20}

Herein, we introduced a novel method to generate a close contact between C\textsubscript{3}N\textsubscript{4} and WO\textsubscript{3} by the reaction of Na\textsubscript{3}WO\textsubscript{4}·2H\textsubscript{2}O and C\textsubscript{3}N\textsubscript{4} under hydrothermal conditions. To enhance the performance, rGO was also used to function as an electron mediator. By calcining a mixture of rGO and melamine, the graphene layer was able to be homogeneously mixed with C\textsubscript{3}N\textsubscript{4} layers. Then through the hydrothermal method, the C\textsubscript{3}N\textsubscript{4}-rGO composites were loaded with WO\textsubscript{3} particles, which function as O\textsubscript{2} evolution photocatalyst. It is demonstrated that the binary (in the case of no rGO) or ternary (in the case of containing rGO) composites were able to give out H\textsubscript{2} and O\textsubscript{2} under visible light irradiation (λ > 420 nm) with relatively high performance when loaded with Pt as co-catalyst, and an appropriate amount of rGO will enhance the performance.

2. Experimental section

Synthesis of C\textsubscript{3}N\textsubscript{4}-rGO composite and pure C\textsubscript{3}N\textsubscript{4}

Graphene oxide was synthesized according to the modified Hummers method as described in our previous work.\textsuperscript{21} The as-prepared GO was then reduced by the hydrothermal method. 60 mg of GO was dissolved in 30 mL of H\textsubscript{2}O by moderate sonication and the pH was adjusted to about 7 using NaOH solution before transferring into a Teflon-lined steel autoclave, which was heated in an oven at 140 °C for 18 h. The obtained rGO was collected and washed with distilled water and ethanol several times, and dried at 90 °C for 2 h. C\textsubscript{3}N\textsubscript{4}-rGO composites were obtained by calcining the mixtures of melamine and rGO with different mass ratios. These C\textsubscript{3}N\textsubscript{4}-rGO composites are noted as C\textsubscript{3}N\textsubscript{4}-rGO-x, where x represents the mass ratio of melamine to rGO during the synthesis process. For example, the composite C\textsubscript{3}N\textsubscript{4}-rGO-150 was prepared by calcining the mixture of 20 mg of rGO and 3000 mg of melamine at 500 °C for 3 h with a 5 °C min\textsuperscript{−1} increasing rate. Pure C\textsubscript{3}N\textsubscript{4} was also obtained by calcining melamine at 500 °C for 3 h.

Synthesis of C\textsubscript{3}N\textsubscript{4}-rGO-WO\textsubscript{3} and C\textsubscript{3}N\textsubscript{4}-WO\textsubscript{3} composites

The ternary composites are noted as C\textsubscript{3}N\textsubscript{4}-rGO-WO\textsubscript{3}-x, WO\textsubscript{3}-m/n, m representing the initial reacting mass of C\textsubscript{3}N\textsubscript{4}-rGO-x in mg, n representing that of Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O. Taking C\textsubscript{3}N\textsubscript{4}-rGO-150-WO\textsubscript{3} 400–260 for example, 400 mg of C\textsubscript{3}N\textsubscript{4}-rGO-150 and 260 mg of Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O (99%, Aldrich) were mixed in 30 mL of deionized water and kept under stirring at ca. 300 rpm for 12 h. Then the pH value was adjusted to 2 using diluted HCl solution. After further stirring at ca. 300 rpm for another 12 h, the suspension was transferred into a Teflon-lined steel autoclave and kept at 160 °C for 18 h. The C\textsubscript{3}N\textsubscript{4}-rGO composite was obtained by the same method except for using pure C\textsubscript{3}N\textsubscript{4} instead of C\textsubscript{3}N\textsubscript{4}-rGO composites. After hydrothermal reaction, the resulted composites were separated by centrifugation at 4000 rpm and washed with distilled water several times before drying at 90 °C for 3 h.

Pt-loading on the C\textsubscript{3}N\textsubscript{4}-rGO, C\textsubscript{3}N\textsubscript{4}-rGO-WO\textsubscript{3} and C\textsubscript{3}N\textsubscript{4}-WO\textsubscript{3} composites

Pt was firstly loaded onto the specimen by impregnation: an appropriate amount of H\textsubscript{2}PtCl\textsubscript{6} solution (ca. 4 mL) was impregnated into the sample powders by evaporating the solvent of the mixed suspension at 90 °C until dry. For the H\textsubscript{2}-evolution test, C\textsubscript{3}N\textsubscript{4}-rGO composites, these Pt-loaded samples were used in the presence of triethanolamine (TEOA) as sacrificial agent. For the overall water splitting test by C\textsubscript{3}N\textsubscript{4}-rGO-WO\textsubscript{3} and C\textsubscript{3}N\textsubscript{4}-WO\textsubscript{3} composites, these Pt-loaded samples were further reduced by NaBH\textsubscript{4} solution in Ar protection. For example, 200 mg of C\textsubscript{3}N\textsubscript{4}-rGO-150-WO\textsubscript{3} 400–260 loaded with 1 wt% Pt was dissolved in 30 mL of deionized water and purged with Ar for 30 min before adding 5 mg of NaBH\textsubscript{4}. After 2 h of reduction, the suspension was centrifuged and washed with distilled water several times. The resulted slurry was then used for photocatalytic tests.

Material characterization

Specimens were characterized by XRD using a PANalytical Empyrean Reflection diffractometer with a Cu Ka source (λ = 1.541 Å). TEM analysis was performed using a JEM-2011. XPS spectra were obtained using an ESCALAB 250 and all binding energies were referenced to the C 1s peak at 284.6 eV. A UV–vis spectrophotometer (JASCO-V550) was used for obtaining the optical absorbance spectra.

Photocatalytic measurement

The measurement was performed with a home-made Teflon reactor with the top window sealed by Pyrex glass. In the H\textsubscript{2}-evolution test by C\textsubscript{3}N\textsubscript{4}-rGO composites loaded with 1 wt% Pt, 200 mg of photocatalyst was dispersed in 100 mL of water and 10 mL of TEOA was added as sacrificial agent. In the O\textsubscript{2}-evolution test by WO\textsubscript{3}·1/3H\textsubscript{2}O, 100 mg of WO\textsubscript{3}·1/3H\textsubscript{2}O was dispersed in 100 mL of water and 10 mL of TEOA was added as sacrificial agent. After the above-mentioned measurements, the water samples were analyzed by gas chromatograph (Shimadzu GC-14B) with Porapak Q column.
powder was dispersed in 100 mL of water with 10 mmol L$^{-1}$ AgNO$_3$ as an electron acceptor. The reactor was firstly purged with pure Ar to remove air from the reaction system, then the solution was irradiated by a 250 W iron doped metal halide UV-vis lamp (UV Light Technology Limited, UK) with a UV cut-off filter ($\lambda > 420$ nm) and the amount of H$_2$ or O$_2$ produced was determined by gas chromatography (Agilent 3000 Micro Gas Chromatograph with a TCD detector, using argon carrier gas). The H$_2$- and O$_2$-evolution half reaction results shown in the ESI† demonstrated their activity under visible light. The mediator-free Z-scheme overall water splitting reaction trials were performed in the same top-irradiation system. During these trials, 200 mg of Pt-loaded C$_3$N$_4$-rGO-WO$_3$ or C$_3$N$_4$-rGO particles was suspended in 100 mL of deionized water, but no TEOA was added. The evolved gas composition in the sealed reactor was measured by gas chromatography.

**Quantum yield efficiency measurement**

The apparent quantum yield (AQY) of the Z-scheme water splitting with a two-photon excitation process was measured using the same reactor with the addition of a band-pass filter (420 nm, $\Delta\lambda_{1/2} = 10$ nm). The AQY values were calculated using the following equation:

$$\text{AQY}(\%) = \frac{4 \times n(H_2)/n(\text{photons})}{100}$$  \hspace{1cm} (1)

where $n(H_2)$ and $n(\text{photons})$ represent the quantities of evolved H$_2$ molecules and the number of incident photons, respectively. The total number of incident photons was determined using a grating spectroradiometer (Apogee Instruments, Inc, Model MQ-200) and the the incident photon power in the apparent quantum yield measurement is about 120 $\mu$mol m$^{-2}$ s$^{-1}$.

**3. Results and discussion**

Fig. 1 shows the typical XRD patterns of WO$_3$ and C$_3$N$_4$-rGO-WO$_3$ composites resulting from the hydrothermal reaction of Na$_2$WO$_4$$\cdot$2H$_2$O without or with different contents of C$_3$N$_4$-rGO-150. The XRD pattern in Fig. 1a denotes the presence of orthorhombic tungsten oxide one third hydrate (WO$_3$$\cdot$1/3H$_2$O, JCPDS card no. 54-1012), and the characteristic peak from C$_3$N$_4$ located at around 27$^\circ$ increased with the increment of C$_3$N$_4$-rGO-150 content, as shown in Fig. 1b and c. There are no obvious diffraction peaks for WO$_3$$\cdot$1/3H$_2$O in Fig. 1c, which may be due to the large molar ratio of C$_3$N$_4$ to WO$_3$ in C$_3$N$_4$-rGO-WO$_3$ 1000–260 (ca. 13.8 calculated from the added amount). If considering the smaller density and bigger particle size of C$_3$N$_4$ than WO$_3$ nanoparticles in C$_3$N$_4$-rGO-WO$_3$ 1000–260, the XRD diffraction density of C$_3$N$_4$ is much stronger than that of WO$_3$ nanoparticles. Therefore, the diffraction peaks of WO$_3$$\cdot$1/3H$_2$O properly overlapped with those of C$_3$N$_4$. In addition, the crystallinity of WO$_3$ may be also poor because of the dispersion of C$_3$N$_4$ particles.

Fig. 2a and b show the TEM images of C$_3$N$_4$-rGO-WO$_3$ 400–260 and C$_3$N$_4$-rGO-WO$_3$ 1000–260, respectively. It is obvious that in the hydrothermal reaction, a higher Na$_2$WO$_4$$\cdot$2H$_2$O/C$_3$N$_4$-rGO-WO$_3$ ratio means that more isolated WO$_3$ particles are not loaded on the surface of C$_3$N$_4$-rGO-150, while in C$_3$N$_4$-rGO-WO$_3$ 1000–260, almost no independent WO$_3$ particles exist. By loading Pt as co-catalyst, efficient H$_2$-evolution performance can be realized. Fig. 2c and S1 (see in ESI†) show the TEM images of C$_3$N$_4$-rGO-WO$_3$ 400–260 loaded with 1 wt% Pt after several periods of photocatalytic water splitting tests, indicating that Pt is mainly distributed onto the surface of C$_3$N$_4$ perhaps due to its stronger ability to chelate Pt$^\text{2+}$. The typical UV-vis light absorbance spectra in Fig. 2d also indicate that there were no obvious differences in the

![Fig. 1 XRD patterns of pure WO$_3$ (a), C$_3$N$_4$-rGO-150-WO$_3$ 400–260 (b) and C$_3$N$_4$-rGO-150-WO$_3$ 1000–260 (c).](image1)

![Fig. 2 TEM images of C$_3$N$_4$-rGO-150-WO$_3$ 400–260 (a), C$_3$N$_4$-rGO-150-WO$_3$ 1000–260 (b), C$_3$N$_4$-rGO-150-WO$_3$ 400–260 loaded with 1 wt% Pt after photocatalytic test (c); the UV-vis light absorbance spectra (converted from the corresponding reflectance spectra) of three typical samples loaded with 1 wt% Pt (d).](image2)
absorbance between the composites with different WO3 contents, while adding rGO indeed increased the absorption toward visible light.

We used the as-prepared C3N4–rGO-150–WO3 400–260 without loading Pt as photocatalyst for the cycling water-splitting test under visible light (Fig. 3). As shown in Fig. 3a, in the initial four cycles, the performance increased but then decayed on further cycling. The best performance is only for the first four cycles, the performance increased but then decayed on further cycling. The best performance is only about 12 μmol of H2 in 20 hours’ irradiation. After loading Pt as co-catalyst, the case is much different, as shown in Fig. 3b. The H2-evolution performance is very stable from the second cycle and the final amount of H2 produced in 20 hours is as high as 35 μmol and the produced O2 is about half in μmol compared with that of H2. It is also noted that without loaded Pt, the photocatalyst underwent an obvious color change during the photo-reaction as shown in Fig. 3c and d, where the milk-white suspension changed into blue after six cycles of test. According to much reported research on the photochromogenic WO3, when irradiated at a photo energy higher than its band gap (2.8 eV), photochromism would occur, in which the photo-generated electron–hole would lead to the reduction of W6+ into blue-colored W5+. While after being loaded with Pt nanoparticles, the photocatalyst became just a little darker compared with that of the milk-white C3N4–rGO-150–WO3 400–260, and no color change occurred during the photo-reaction, as shown in Fig. 3e. It was discovered that the loaded Pt was able to inhibit the color change, which may be due to the efficient electron capture by the loaded Pt nanoparticles. The gas generation amount dependence on reaction time shown in Fig. S2† for C3N4–rGO-150–WO3 400–260 loaded with 1 wt% Pt indicates that gaseous products evolve linearly for the next 12 h in a ratio of ca. 2:1 (H2 and O2: 1.52 and 0.74 μmol h−1) under visible light.

To investigate the effects of graphene content, the mass ratio of C3N4 (or C3N4–rGO) and WO3, the pH in the photocatalytic system and the amount of loaded Pt on the water-splitting performance, we tested the H2/O2 evolution amount with different photocatalysts and in different conditions. As indicated by no. 1 and 2 in Table 1, when using only C3N4 loaded with 1 wt% Pt in nonsacrificial conditions, no water splitting occurred, while when using C3N4–rGO-150 composite loaded with 1 wt% Pt, the produced H2 is about 3.3 μmol in 20 hours’ irradiation. In Jorge et al.’s work, C3N4 was used for H2 and O2 evolution from water half-splitting with methanol and Ag+ as sacrificial agent, respectively. In our photocatalytic reaction test, no. 2, the little water splitting activity should come from the reduction and oxidation of water due to the improved electron–hole separation by graphene. In no. 3–6, it is also shown that different rGO contents in the C3N4–rGO composites have a great effect on the water-splitting activity. Both no rGO and too much rGO in the C3N4–rGO composites give worse performance for the H2/O2 evolution than that in the C3N4–rGO-150 composite (no. 3), even though the C3N4–rGO-150 composite only displays an enhancement of 15.8% for the H2/O2 evolution over the pure C3N4 and WO3 system (no. 6). We have also investigated the rGO effect by testing the H2-evolution performance using different C3N4–rGO composites with TEOA as sacrificial agent and Pt as co-catalyst (more details in Fig. S3 and Table S1 in ESI†). It is implied that rGO has two synergistic effects, one is to prevent the hole–electron recombination by transferring electrons, and the other is to prevent the efficient irradiation due to its opacity and light scattering. An appropriate amount of graphene in the C3N4–rGO composite would improve the electron transfer and further prevent the charge carrier-recombination, thus a little enhancement occurred for C3N4–rGO-150 composite with Pt as co-catalyst.

The results for no. 3 and 8 in Table 1 show that sample C3N4–rGO-150–WO3 1000–260 displays a higher performance by 37% than C3N4–rGO-150–WO3 400–260 under the same conditions (i.e., loaded with 1 wt% Pt in pH = 7), indicating that too much WO3 deposited on the surface of C3N4–rGO-150 will prevent the incident light from reaching the C3N4–rGO-150 surface, which results in the weakened photoexcitation of C3N4–rGO-150. However, for the pure C3N4 and WO3 system, there is no obvious change in the water-splitting performance with different mass ratios of C3N4 to WO3 (no. 6 and 7 in Table 1). These results show that the WO3 amount has a more obvious influence on the C3N4–rGO-150 system than the pure C3N4 system, further suggesting that rGO is able to play a significant role in the Z-scheme water-splitting system because of its good conductivity and its function as promising electron mediator for transferring the photo-generated electrons from WO3 to the photo-generated holes in C3N4. The effect of the loaded Pt amount is also revealed from a comparison between no. 5 and 9 or no. 3 and 10.
When the pH equals 3, the produced H2 is as low as 11.4 μmol in 20 hours. Since WO3 is inherently unstable at high pH, we did not test the performance under higher pH conditions.8,11 In our case, the effect of pH on the water-splitting activity was also investigated using C3N4-rGO-150-WO3 1000-260 as target. It is found that with increasing pH, the gas evolution rate is gradually increased (no. 8, 11). Thus the pH effect should not come from the aggregated negative effect for the O2 evolution would trade off the gas evolution, as proved by other reports.37–39

According to previous research on the Z-scheme photocatalyst system, to ensure the charge transfer, intimate physical interaction between the two photocatalysts was often realized by the aggregation of the two photocatalysts under some appropriate pH.8,11 In our case, the effect of pH on the water-splitting activity was also investigated using C3N4-rGO-150-WO3 1000-260 as target. It is found that with increasing pH, the gas evolution rate is gradually increased (no. 8, 11–14). When the pH equals 3, the produced H2 is as low as 11.4 μmol in 20 hours. Since WO3 is inherently unstable at high pH, we did not test the performance under higher pH conditions. Thus the pH effect should not come from the aggregation level but from the kinetic rate of the H2 and O2 evolution reactions, which can be expressed as the following:

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \tag{2}
\]

\[
2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \tag{3}
\]

It can be inferred that although pH has the conflicting effect for eqn (2) and (3), a higher pH is beneficial to the whole performance. This is despite that under acidic conditions, H2-evolution reaction is relatively favorable, the associated negative effect for the O2 evolution would trade off the little benefit since the water oxidation depends on the adsorbed OH− ions onto the WO3 surface and their following oxidation by multiple photo-generated holes.40 Thus under more alkaline conditions, the final H2/O2-evolution performance turns out to be higher, and these results indicate that the O2-evolution reaction is the rate-determining process.

We also prepared a C3N4-WO3 composite via two other methods, one by calcining WO3 nanoparticles and C3N4 mixture at 350 °C and the other by hydrothermal treatment of WO3 nanoparticles and C3N4 mixture at 160 °C. Both of the as-prepared mixtures were loaded with 1 wt% Pt before the photocatalytic test. And for the two cases, no H2 was detected. It is confirmed that the hydrothermal conditions result in the intimate contact between C3N4 (or C3N4-rGO) and WO3 due to the special high-temperature and high-pressure environment. And the in situ formation of WO3 particles on the C3N4 framework also contributes to the intimate interaction between the two photocatalysts.

It is worthy to note that the photocatalysts used in Table 1 were fresh wet samples from the reduction by NaBH4 without drying. And we also tried to dry the sample C3N4-rGO-150-WO3 1000-260 (loaded with 1 wt% Pt) after several cycling tests with stable performance. Interestingly, after drying in air at 80 °C for 4 hours, the sample showed a lower activity than its stable performance before drying, and only after 3 cycles, was the performance recovered, as shown in Fig. 4. Then the sample was dried again at 80 °C for 30 hours, after which the H2/O2 evolution became even worse, and also recovered after 4 cycles (Fig. 4a). We investigated the XPS of the sample dried in air at 80 °C for 30 hours and the fresh wet sample dried in Ar. The XPS survey spectrum shown in Fig. S4 (see in ESI†) demonstrated the existence of C, N, O, Pt and W, but no Na was observed. Although both of the samples showed a high content of PtOx (indicated by the Pt 4f7/2 and Pt 4f5/2 peaks centered at ca. 73.0 eV and 76.3 eV, respectively),41 the metallic Pt content in the sample dried in Ar is obviously higher than that dried in air (indicated by the Pt 4f7/2 and Pt 4f5/2 peaks centered at ca. 71.0 eV and 74.3 eV, respectively), as shown in Fig. 4b and c.42 Therefore, it is inferred that the evolved H2 would reduce PtOx into Pt metal during the irradiation and the activity of the sample is quite sensitive to the Pt metal content.

### Table 1 Overall water splitting under visible light by C3N4-WO3 system in the presence and absence of rGO

<table>
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<th>No.</th>
<th>Type of C3N4 or C3N4-rGO</th>
<th>C3N4 or C3N4-rGO (mg)</th>
<th>Na2WO4/2H2O (mg)</th>
<th>Amount of loaded Pt</th>
<th>pH</th>
<th>Activity after 20 h irradiation</th>
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<tr>
<td>14</td>
<td>C3N4-rGO-150</td>
<td>1000</td>
<td>260</td>
<td>1 wt% Pt</td>
<td>8</td>
<td>33.5</td>
</tr>
</tbody>
</table>

a Conditions: photocatalyst (200 mg in total) in water (100 mL); light source, 250 W iron-doped metal halide ultraviolet-visible lamp, with a cut-off filter (λ > 420 nm); top-irradiation cell with a quartz glass. b Pt was loaded firstly by impregnation of H2PtCl6, then lateral reduction with NaBH4 solution and lastly washing several times before using as photocatalyst in slurry. c The pH of the suspension in the photocatalytic test system.
The evolution of \( \text{H}_2 \) from water splitting was further confirmed by using \( \text{D}_2\text{O} \) as the solvent in the suspension of photocatalyst. The evolved gas mixture was then detected by the mass spectra and the results are shown in Fig. S5 (see in ESI†). The extra signal located at 4 amu is due to evolved \( \text{D}_2 \), which is absent in that of the background gas. We also measured the apparent quantum yield efficiency under monochromatic light at 420 nm. The sample \( \text{C}_3\text{N}_4\text{-rGO-150-WO}_3 \text{1000–260} \) (loaded with 1 wt\% Pt) under neutral conditions shows an AQY efficiency of ca. 0.9\% while the homologous sample without rGO shows a smaller value (i.e., 0.7\%), further demonstrating the positive effect of rGO.

Although Martin et al.\textsuperscript{10} recently reported a similar Z-scheme water splitting on the basis of \( \text{C}_3\text{N}_4 \) and \( \text{WO}_3 \) (or \( \text{BiVO}_4 \)), their performance is strongly dependent on the redox mediator type (i.e., \( \Gamma/\text{IO}_3^- \)) and the pH. However, in our \( \text{C}_3\text{N}_4\text{-rGO} \) (or \( \text{C}_3\text{N}_4 \)) and \( \text{WO}_3 \) composite system, no redox mediator is needed for the water-splitting photocatalytic test, which further infers that the intimate contact resulting from hydrothermal conditions is of benefit to the \( \text{H}_2/\text{O}_2 \) evolution in the two-step photoexcitation Z-scheme system. Fig. 5 shows a tentatively proposed mechanism for the \( \text{H}_2/\text{O}_2 \) evolution by \( \text{C}_3\text{N}_4\text{-WO}_3 \) composite with or without the mediation of rGO.

Considering the Pt function as discussed above, \( \text{H}_2 \) is more readily evolved from the surface of Pt than that of \( \text{C}_3\text{N}_4 \). Therefore, water is oxidized by the photo-induced holes in the VB of \( \text{WO}_3 \) and reduced by the electrons on Pt trapped from the CB of \( \text{C}_3\text{N}_4 \). The electrons on CB of \( \text{WO}_3 \) are able to combine with the holes in VB of \( \text{C}_3\text{N}_4 \) at the interface due to the intimate contact. rGO successfully functions as a positive electron mediator because of its good conductivity for electron migration, its sturdy contact with \( \text{C}_3\text{N}_4 \) resulted from its calcination with the precursor (i.e., melamine), and its good contact with \( \text{WO}_3 \) particles under the hydrothermal conditions.

4. Conclusions

In summary, we have introduced a mediator-free Z-scheme system design based on \( \text{C}_3\text{N}_4 \) by utilizing \( \text{WO}_3 \) as \( \text{O}_2 \) photocatalyst for the first time, where \( \text{C}_3\text{N}_4 \) and \( \text{WO}_3 \) are combined as composites through a facile hydrothermal method. Successful water splitting under visible light (\( \lambda > 420 \text{ nm} \)) can be realized without any redox mediator when Pt is loaded on the surface of the composites. More importantly, rGO is introduced into these composites to form \( \text{C}_3\text{N}_4\text{-rGO-WO}_3 \) composites and this shows a positive effect on the performance in an optimized amount. The highest \( \text{H}_2/\text{O}_2 \) evolution rates are about 2.84 and 1.46 \( \mu\text{mol h}^{-1} \) under visible light (\( \lambda > 420 \text{ nm} \)) with a quantum yield of 0.9\% at 420 nm. Although the resulting performance is not in the highest for water splitting, the newly proposed methodology for constructing heterostructures through the hydrothermal method will pave the way for more efficient overall water splitting with two-step photoexcitation Z-scheme systems in the absence of a redox mediator.
Acknowledgements

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Notes and references

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