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ARTICLE TYPE

Facile Structure Design Based on C₃N₄ for Mediator-free Z-Scheme Water Splitting under Visible Light

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In this work, two photocatalysts (i.e., C_3N_4 and WO_3) were successfully combined into a heterojunction structure by a facile hydrothermal method for mediator-free overall water splitting, analogous to the natural photosynthesis over two-photo excited Z-scheme system. Hydrogen and oxygen are evolved with a 2:1 ratio by irradiating the C_3N_4 -WO₃ composites loaded with Pt under visible light ($\lambda > 420$ nm) without any redox mediator. Introducing reduced graphene oxide (rGO) to the C_3N_4 -WO₃ composites enhances the water splitting efficiency. Through optimizing the mass ratio in the C_3N_4 -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 quantum yield of 0.9%. Our findings demonstrate that hydrothermal method is a promising strategy for constructing intimate heterostructures for Z-scheme 15 water-splitting system without using any redox mediator, and that rGO can be used to further enhance the performance in optimized conditions.

1. Introduction

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With the increasing energy demand and concerns about environmental issues, hydrogen gas is considered as a promising ²⁰ fuel because of its no carbon emission nor other harmful byproducts.¹ 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 ²⁵ the most similar to natural photosynthesis.²⁻⁶ Normally, a Z-

scheme system contains two photocatalysts (one for H_2 evolution, and the other for O_2 evolution) and usually an electron mediator, which transfers the electrons from the excited O_2 photocatalyst to the holes generated in the H_2 photocatalyst.⁷

³⁰ It is suggested that electron transfer is the rate-determining process.⁸ The commonly used electron mediators are ionic redox couples such as $IO_3^{-}/I^{-,2, 3, 9}$ or Fe³⁺/Fe^{2+,4,9,10} Compared with these ionic redox couples, solid electron shuttle is more advanced for the recycle of the photocatalyst and cleaning of water. The

³⁵ challenges for the efficient H₂/O₂ evolution lie in the electronaccepting and -donating abilities of the mediator, which should retain a dynamic equilibrium and keep stable during reactions.¹¹ Furthermore, interface contact in the ternary system also plays an important role in maintaining continuous electron flow between

- ⁴⁰ the two photocatalysts. Considering the extremely high conductivity and specific surface area of graphene, it may be a good candidate as electron mediator for Z-scheme system.¹¹ Besides, it is also challenging to choose appropriate photocatalysts for realizing the intimate physical interaction with
- ⁴⁵ graphene, the efficient charge carrier separation, the H_2/O_2 evolution on the H_2/O_2 photocatalysts and then finally preventing water formation due to the backward reaction of H_2 and O_2 .^{12, 13}

In Iwase et al's report,¹¹ it has been shown that photoreduced graphene oxide (PRGO) was able to function as a solid electron 50 mediator for Z-scheme overall water splitting, where SrTiO3:Rh was used as H₂ evolution photocatalyst, with 0.7 wt% Ru as cocatalyst, 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 55 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 the neutral condition, the performance is much lower, which is considered due to the bad physical interaction between the PRGO/BiVO4 and 60 Ru/SrTiO3:Rh under neutral conditions. In total, the reported Zscheme 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.⁸ reported the interparticle electron transfer 65 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/SrTiO3:Rh and BiVO4. Thus, more sturdy contacts between the H_2/O_2 evolution phototcatalysts need to be 70 found.

Since the introduction of graphitic carbon nitride (C_3N_4) into heterogeneous catalysis in 2006,^{14, 15} this yellow polymer consisting of tri-s-triazines interconnected via tertiary amines has attracted increasing interest in material research especially in H₂-⁷⁵ evolution photocatalysis under visible light.¹⁶⁻¹⁸ The band gap of C_3N_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.^{16, 19} More importantly, the preparation of C_3N_4 is

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low cost since it only consists two elements (C and N). For O_2 evolution photocatalysis from water, tungsten trioxide (WO₃) has been widely investigated because of its suitable bandgap, high electron mobility, abundance and low cost.²⁰

- ⁵ Herein, we introduced a novel method to generate a close contact between C₃N₄ and WO₃ by the reaction of Na₂WO₄·2H₂O and C₃N₄ under hydrothermal conditions. To enhance the performance, rGO was also used to function as electron mediator. By calcining the mixture of rGO and melamine, the graphene
- ¹⁰ layer was able to be homogeneously mixed with C_3N_4 layers. Then through hydrothermal method, the C_3N_4 -rGO composites were loaded with WO₃ particles, which function as O₂ evolution photocatalyst. It is demonstrated that the binary (in the case of no rGO) or ternary (in the case of containing rGO) composites were ¹⁵ able to give out H₂ and O₂ under visible light irradiation ($\lambda > 420$ nm) with relatively high performance when loaded with Pt as cocatalyst, and appropriate amount of rGO will enhance the performance.

2. Experimental Section

- ²⁰ Synthesis of C_3N_4 -rGO composite and pure C_3N_4 : Graphene oxide was synthesized according to the modified Hummers method as described in our previous work.²¹ The as-prepared GO was then reduced by hydrothermal method. 60 mg of GO was dissolved in 30 mL of H₂O by moderate sonication and the pH was adjusted to 25 about 7 using NaOH solution before transferred into a Teflonlined 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. C₃N₄rGO composites were obtained by calcining the mixtures of 30 melamine and rGO with different mass ratios. These C₃N₄-rGO composites are noted as C_3N_4 -rGO-x, where x represents the mass ratio of melamine to rGO during the synthesis process. For example, the composite C₃N₄-rGO-150 was prepared by calcining the mixture of 20 mg of rGO and 3000 mg of melamine at 500 °C 35 for 3 h with a 5 °C/min increasing rate. Pure C₃N₄ was also obtained by calcining melamine at 500 °C for 3 h.
- Synthesis of C_3N_4 -rGO-WO₃ and C_3N_4 -WO₃ composites: The ternary composites are noted as C_3N_4 -rGO-x-WO₃ m-n, m representing the initial reacting mass of C_3N_4 -rGO-x in mg, n
- ⁴⁰ representing that of Na₂WO₄·2H₂O. Taking C₃N₄-rGO-150-WO₃ 400-260 for example, 400 mg of C₃N₄-rGO-150 and 260 mg of Na₂WO₄·2H₂O (99%, Aldrich) were mixed in 30 mL of deionized water and kept stirring at ca. 300 rpm for 12 h. Then the pH value was adjusted to 2 using diluted HCl solution. After ⁴⁵ 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 C₃N₄-WO₃ composite was obtained by the same method except for using pure C₃N₄ instead of C₃N₄-rGO composites. After hydrothermal reaction, the resulted composites ⁵⁰ were separated by centrifugation at 4000 rpm and washed with
- distilled water for several times before dried at 90 °C for 3 h. *Pt-loading on the* C_3N_4 -*rGO*, C_3N_4 -*rGO*-*WO*₃ and C_3N_4 -*WO*₃
- *composites*: Pt was firstly loaded onto the specimen by impregnation method: proper amount of H₂PtCl₆ solution (ca. 4 ⁵⁵ mL) was impregnated into the sample powders by evaporating the solvent of the mixed suspension at 90 °C until dry. For H₂-

evolution test by C₃N₄-rGO composites, these Pt-loaded samples

- O_3) hassacrificial agent. For overall water splitting test by C_3N_4 -rGO-p, high60 WO_3 and C_3N_4 -WO_3 composites, these Pt-loaded samples were
further reduced by NaBH₄ solution in Ar protection. For example,
200 mg of C_3N_4 -rGO-150-WO_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 NaBH₄. After 2 h for reduction, 65 the suspention was centrifugated and washed with distilled water for several times. The resulted slurry was then used for photocatalytic test.

were used in the presence of triethanolamine (TEOA) as

Material Characterizations: Specimens were characterized by XRD on a PANalytical Empyrean Reflection diffractometer with a Cu K α source ($\lambda = 1.541$ Å). TEM analysis was performed on a JEM-2011. XPS were tested by 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 testing the optical absorbance spectra.

- Photocatalytic measurement: The measurement was performed with a home-made Teflon reactor with top window sealed by a pyrex glass. In H₂-evolution test by C₃N₄-rGO composites loaded with 1 wt% Pt, 200 mg of photocatalyst was dispersed into 100 mL of water and 10 mL of TEOA was added as sacrificial agent.
- ⁸⁰ In O₂-evolution test by WO₃· 1/3H₂O, 100 mg of WO₃· 1/3H₂O powder was dispersed into 100 mL of water with 10 mmol/L of AgNO₃ 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-
- ss Vis lamp (UV Light Technology Limited, UK) with a UV cut-off filter ($\lambda > 420$ nm) and the amount of H₂ or O₂ produced was determined by gas chromatography (Agilent 3000 Micro Gas Chromatograph with a TCD detector, using argon carrier gas). The H₂- and O₂-evolution half reaction results shown in
- ⁹⁰ supporting information 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 C₃N₄-rGO-WO₃ or C₃N₄-WO₃ composites were suspended in 100 mL of deionized water, but no ⁹⁵ 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:²²

AQY (%) = $[4 \times n(H_2)]/n(\text{photons}) \times 100$ (1)

where $n(H_2)$ and n(photons) represent the quantities of evolved H_2 molecules and the number of incident photons, respectively. ¹⁰⁵ The total number incident photons were 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 µmol m⁻² s⁻¹.

3. Results and Discussion

¹¹⁰ Figure 1 shows the typical XRD patterns of WO₃ and C₃N₄-rGO-150-WO₃ composites resulting from the hydrothermal reaction of Na₂WO₄· 2H₂O without or with different contents of C₃N₄-rGO-150. The XRD pattern in Figure 1a denotes the presence of orthorhombic tungsten oxide one third hydrate (WO₃· 1/3H₂O, Published on 28 April 2015. Downloaded by Gazi Universitesi on 04/05/2015 12:35:25

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JCPDS Card no. 54-1012), and the characteristic peak from C_3N_4 located at around 27 degree increased with the increment of C_3N_4 -rGO-150 content, as shown in Figure 1b and 1c. There are no obvious diffraction peaks for $WO_3 \cdot 1/3H_2O$ in Figure 1c, ${}_5$ which may be due to the large molar ratio of C_3N_4 to WO_3 in C_3N_4 -rGO-150-WO_3 1000-260 (ca. 13.8 calculated from the

added amount). If considering the smaller density and bigger particle size of C_3N_4 than WO₃ nanoparticles in C_3N_4 -rGO-150-WO₃ 1000-260, the XRD diffraction density of C_3N_4 is much ¹⁰ stronger than that of WO₃ nanoparticles. Therefore, the diffraction peaks of WO₃·1/3H₂O were properly overlapped by that of C_3N_4 . In addition, the crystallinity of WO₃ may be also poor because of the dispersion of C_3N_4 particles.



 Figure 1. XRD patterns of pure WO₃ (a), C₃N₄-rGO-150-WO₃ 400-260 (b) and C₃N₄-rGO-150-WO₃ 1000-260 (c).



Figure 2. TEM images of C₃N₄-rGO-150-WO₃ 400-260 (a), C₃N₄-rGO-150-WO₃ 1000-260 (b), C₃N₄-rGO-150-WO₃ 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).

Figure 2a and 2b show the TEM images of C₃N₄-rGO-150-WO₃ 400-260 and C₃N₄-rGO-150-WO₃ 1000-260, respectively. It ²⁵ is obvious that in the hydrothermal reaction, the higher Na₂WO₄·2H₂O/C₃N₄-rGO-150 ratio means that the more WO₃

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particles are not loaded on the surface of C_3N_4 -rGO-150 but must be independent of it, while in C_3N_4 -rGO-150 1000-260, almost no independent WO₃ particles exist. By loading Pt as co-catalyst, ³⁰ efficient H₂-evolution performance can be realized. Figure 2c and Figure S1 (see in Supporting Information) show the TEM images of C_3N_4 -rGO-150 400-260 loaded with 1 wt% Pt after several periods of photocatalytic water splitting tests, indicating that Pt is mainly distributed onto the surface of C_3N_4 maybe due to its ³⁵ stronger chelating ability to Pt⁺. The typical UV-Vis light absorbance spectra in Figure 2d also indicate that there were no obvious differences in the absorbance between the composites with different WO₃ contents, while adding rGO indeed increased the absorption toward the visible light.



Figure 3. The performance of the cycling test for C_3N_4 -rGO-150-WO₃ 400-260 without (a) and with (b) Pt under pH = 7; the C_3N_4 -rGO-150-WO₃ 400-260 without Pt before photo-reaction (c) and after six cycle of photo-reaction (d); the sample C_3N_4 -rGO-150-WO₃ 400-260 with Pt after six cycles of photo-reaction (e).

We used the as-prepared C₃N₄-rGO-150-WO₃ 400-260 without loading Pt as photocatalyst for cycling water-splitting test under visible light (Figure 3). As shown in Figure 3a, in the initial four cycles, the performance increased but then decayed on further 50 cycling. The best performance is only about 12 µmol H₂ in 20 hours' irradiation. After loading Pt as co-catalyst, the case is much different, as shown in Figure 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 $_{55}$ produced O₂ is about half in µmol compared with that of H₂. It is also noted that without loaded Pt, the photocatalyst underwent obvious color change during the photo-reaction as shown in Figure 3c and 3d, where the milk-white suspension changed into blue after six cycles of test. According to much reported research 60 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 W^{5+, 23-28} While after loaded with Pt nanoparticles, the photocatalyst became just a little darker 65 comparing with that of the milk-white C₃N₄-rGO-150-WO₃ 400-260, and no color changed during the photo-reaction, as shown in

No.	Hydrothermal conditions			_		Activity after 20 h irradiation	
	Type of C ₃ N ₄ or C ₃ N ₄ -rGO	C ₃ N ₄ or C ₃ N ₄ -rGO (mg)	Na ₂ WO ₄ ·2H ₂ O (mg)	Amount of loaded Pt ^b	pH ^c	H ₂ (µmol)	O2 (µmol)
1	Pure C ₃ N ₄	400	0	1 wt% Pt	7	trace	Trace
2	C ₃ N ₄ -rGO-150	400	0	1 wt% Pt	7	3.3	1.1
3	C ₃ N ₄ -rGO-150	400	260	1 wt% Pt	7	35.1	18.5
4	C ₃ N ₄ -rGO-80	400	260	1 wt% Pt	7	26.1	14.1
5	C ₃ N ₄ -rGO-50	400	260	1 wt% Pt	7	20.8	11.2
6	Pure C ₃ N ₄	400	260	1 wt% Pt	7	30.3	14.8
7	Pure C ₃ N ₄	1000	260	1 wt% Pt	7	29.9	14.5
8	C ₃ N ₄ -rGO-150	1000	260	1 wt% Pt	7	48.1	24.5
9	C ₃ N ₄ -rGO-50	400	260	3 wt% Pt	7	6.0	3.3
10	C ₃ N ₄ -rGO-150	400	260	3 wt% Pt	7	11.0	5.0
11	C ₃ N ₄ -rGO-150	1000	260	1 wt% Pt	3	11.4	30.5
12	C ₃ N ₄ -rGO-150	1000	260	1 wt% Pt	5	29.0	15.1
13	C ₃ N ₄ -rGO-150	1000	260	1 wt% Pt	8	53.5	26.8
14	C ₃ N ₄ -rGO-150	1000	260	1 wt% Pt	10	56.6	29.2

^{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 ($\lambda > 420$ nm); top-irradiation cell with a quartz glass. ^{b)} Pt was loaded by first impregnation of H₂PtCl₆, the lateral reduction with NaBH₄ solution and the last washing for several times before using as photocatalyst in muddy; ^{c)} The pH of the suspension in the photocatalystic test system.

⁵ Figure 3e. It is now discovered that the loaded Pt is able to inhibit the color changing, which may be due to the efficient electron capture by the loaded Pt nanoparticles. The gas generation amount dependence on reaction time shown in Figure S2 for C_3N_4 -rGO-150-WO₃ 400-260 loaded with 1 wt% Pt indicates that ¹⁰ gaseous products evolve linearly for the next 12 h with 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 C_3N_4 (or C_3N_4/rGO) and WO₃, the pH in the photocatalytic system and the amount of loaded Pt on the water-splitting ¹⁵ 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 C_3N_4 loaded with 1 wt% Pt in the nonsacrificial condition, no water splitting occurred, while when using C_3N_4 -rGO-150 composite loaded with 1 wt% Pt, the ²⁰ produced H₂ is about 3.3 µmol in 20 hours' irradiation. In Jorge et al's work, C_3N_4 was used for H₂ and O₂ evolution from water half-splitting with methanol and Ag⁺ as sacrificial agent, respectively.²⁹ In our photocatalytic reaction test, No. 2, the little water splitting activity should come out from the reduction and

- $_{25}$ oxidation of water due to the improved electro-hole separation by graphene. In No. 3-6, it is also shown that different rGO contents in the C₃N₄-rGO composites have great effect on the water-splitting activity. Both no rGO or too much rGO in the C₃N₄-rGO composites gives worse performance for the H₂/O₂ evolution than
- ³⁰ that of the C_3N_4 -rGO-150 composite (No. 3), even though the C_3N_4 -rGO-150 composite only displays an enhancement of 15.8% for the H_2/O_2 evolution over pure C_3N_4 and WO₃ system (No. 6). We have also investigated the rGO effect by testing the H_2 -evolution performance using different C_3N_4 -rGO composites
- ³⁵ using TEOA as sacrificial agent and Pt as co-catalyst (see more details in Figure S3 and Table S1 in Supporting Information). It is implied that rGO has two synergetic effects, one is to prevent the hole-electron recombination by transferring electrons, the other is to prevent the efficient irradiation due to its opacity and light

- ⁴⁰ scattering.³⁰⁻³² An appropriate amount of graphene in the C_3N_4 rGO composite would improve the electron transfer and further prevent the charge carrier-recombination,³³⁻³⁵ thus a little enhancement occurred for C_3N_4 -rGO-150 composite with Pt as co-catalyst.
- The results for No. 3 and 8 in Table 1 show that sample C₃N₄-45 rGO-150-WO₃ 1000-260 displays a higher performance by 37% than that of C₃N₄-rGO-150-WO₃ 400-260 under the same condition (i.e., loaded with 1 wt% Pt in pH = 7), indicating too much WO₃ deposited on the surface of C₃N₄-rGO-150 will ⁵⁰ prevent the incident light reaching to the C₃N₄-rGO-150 surface, which results in the weakened photoexcitation of C₃N₄-rGO-150.³⁶ However, for pure C_3N_4 and WO_3 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 55 results show that WO₃ amount has more obvious influence in C₃N₄-rGO-150 system than pure C₃N₄ system, further suggesting that rGO is able to play a significant role in the Z-scheme watersplitting system because of its good conductivity and its function as promising electron mediator for transferring the photo-60 generated electrons from WO₃ to the photo-generated holes in C₃N₄. The effect of loaded Pt amount is also revealed from comparison between No. 5 and 9 or No. 3 and 10. Too much Pt has negative effect for the gas evolution, as proved by other reports.37-39

According to previous research on 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 the increasing of pH, the gas evolution rate is gradually increased (No. 8, 11-14). When the pH equals to 3, the produced H₂ is as low as 11.4 µmol in 20 hours. Since WO₃ is inherently instable at high pH, we did not test the performance

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under higher pH conditions. Thus the pH effect should not come from the aggregation level but from the kinetic rate of the H_2 and O_2 evolution reactions, which can be expressed as followings:

(2)

$$2H^+ + 2e^- \rightarrow H_2$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

 $_{5}$ $2H_{2}O + 4h^{+} \rightarrow O_{2} + 4H^{+}$ (3) It can be inferred that although pH has the conflicting effect for Equation 2 and 3, a higher pH is beneficial to the whole performance. This is despite that under acidic condition, H₂evolution reaction is relatively favorable, the associated negative effect for the O avolution would trade off the little hencit cines

¹⁰ effect for the O_2 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 photogenerated holes.⁴⁰ Thus under more alkaline conditions, the final H₂/O₂-evolution performance turns out higher, and these results ¹⁵ indicate that the O₂-evolution reaction is the rate-determining process.

We also prepared a C_3N_4 -WO₃ composite via two other methods, one by calcining WO₃ nanoparticles and C_3N_4 mixture at 350 °C and the other by hydrothermal treatment of WO₃ ²⁰ nanoparticles and C_3N_4 mixture at 160 °C. Both of the asprepared mixture were loaded with 1 wt% Pt before photocatalytic test. And for the two cases, no H₂ was detected. It is confirmed that the hydrothermal condition results in the intimate contact between C_3N_4 (or C_3N_4 -rGO) and WO₃ due to ²⁵ the special high-temperature and high-pressure environment. And the *in-situ* formation of WO₃ particles on C_3N_4 framework also contributes the intimate interaction between the two photocatalysts.



³⁰ Figure 4. The cycling performance of the sample $(C_3N_4$ -rGO-150-WO₃ 1000-260 loaded with 1 wt% Pt) dried after several photo-test cycles as fresh slurry (a); XPS of the sample dried in air for 30 hours (b); XPS of the fresh wet sample dried in Ar (c).

It is worth to note that the photocatalysts used in Table 1 were ³⁵ fresh wet samples from the reduction by NaBH₄ without drying. And we also tried to dry the sample C_3N_4 -rGO-150-WO₃ 1000-

260 (loaded with 1 wt% Pt) after several cycling tests with stable performance. Interestingly, after dried in air at 80 °C for 4 hours, the sample showed a lower activity compared with its stable 40 performance before drying, and only after 3 cycles, the performance was recovered, as shown in Figure 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 (Figure 4a). We investigated the XPS of the sample dried 45 in air at 80 °C for 30 hours and the fresh wet sample dried in Ar. The XPS survey spectrum shown in Figure S4 (see in Supporting Information) 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 PtO_x (indicated by the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks ⁵⁰ 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 Figure 4b and 4c.⁴² Therefore, it is inferred that the evolved H₂ would reduce 55 PtOx into Pt metal during the irradiation and the activity of the sample is quite sensitive to the Pt metal content.

The evolution of H₂ from water splitting was further confirmed by using D₂O as the solvent in the suspension of photocatalyst. The evolved gas mixture was then detected by the mass spectra ⁶⁰ and the results were shown in Figure S5 (see in Supporting Information). The extra signal located at 4 amu is due to evolved D₂, 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 C₃N₄-rGO-150-WO₃ ⁶⁵ 1000-260 (loaded with 1 wt% Pt) under neutral condition 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.,¹⁰ recently reported a similar Z-scheme ⁷⁰ water splitting on the base of C_3N_4 and WO_3 (or $BiVO_4$), their performance is strongly dependent on the redox mediator type (i.e., Γ/IO_3) and the pH. However, in our C_3N_4 -rGO (or C_3N_4) and WO_3 composite system, no redox mediator is needed for the water-splitting photocatalytic test, which further infers that the ⁷⁵ intimate contact resulted from hydrothermal condition is of benefit to the H₂/O₂ evolution in the two-photo excited Z-scheme system. Figure 5 shows a tentatively proposed mechanism for the H₂/O₂ evolution by the C_3N_4 -WO₃ composite with or without the mediating of rGO. According to previous study, the CB and VB ⁸⁰ positions of WO₃ are located about +0.41 eV and +3.18 eV,⁴³

while those of C_3N_4 are about +0.41 eV and +5.18 eV, while those of C_3N_4 are about -1.13 eV and +1.57 eV.¹⁹ It is not difficult to infer that under irradiation, O_2 could be evolved from WO₃ surface and H₂ from C_3N_4 surface. Considering the Pt function as discussed above, H₂ is more readily evolved from the surface of Pt than that of C_3N_4 . Therefore, water is oxidized by the photo-induced holes in the VB of WO₃ and reduced by the electrons on Pt trapped from the CB of C_3N_4 . The electrons on CB of WO₃ are able to combine with the holes in VB of C_3N_4 at the interface due to the intimate contact. rGO successfully ⁹⁰ functions as a positive electron mediator because of its good conductivity for electron migration, its sturdy contact with C_3N_4 resulted from its calcination with the precursor (i.e., melamine), and its good contact with WO₃ particles under the hydrothermal conditions.

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Figure 5. Proposed mechanism for the H_2/O_2 evolution by C_3N_4 - WO_3 composite with or without the mediating of rGO.

4. Conclusions

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5 In summary, we have introduced a mediator-free Z-scheme system design based on C_3N_4 by utilizing WO₃ as O_2 photocatalyst for the first time, where C3N4 and WO3 are combined as composites through a facile hydrothermal method. Successful water splitting under visible light ($\lambda > 420$ nm) can be 10 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 C₃N₄-rGO-WO₃ composites and this shows positive effect on the performance in an optimized amount. The highest H_2/O_2 evolution rate is about 2.84 and 1.46 15 μ mol h⁻¹ under visible light ($\lambda > 420$ nm) with the quantum yield of 0.9% at 420 nm. Although the resulted performance is not in the highest level for water splitting, the newly proposed for constructing heterostructure methodology through hydrothermal method will pave a way for more efficient overall 20 water splitting with two-photo excited Z-scheme system in the absence of redox mediator.

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Notes and references

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- \dagger Electronic Supplementary Information (ESI) available: [H₂ evolution performance by C₃N₄-rGO composites with TEOA as sacrificial agent under visible light, rGO contents in different C₃N₄-rGO composites, and the mass spectra results using D₂O]. See DOI: 10.1039/b000000x/
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A mediator-free Z-scheme overall water splitting photocatalyst system is achieved through the use of C_3N_4 (H₂ generation catalyst) and WO₃ (O₂ generation catalyst) composite from a hydrothermal method, and Pt as co-catalyst under visible light ($\lambda > 420$ nm).

