Accepted Manuscript

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PII: S1385-8947(15)01491-6
DOI: <http://dx.doi.org/10.1016/j.cej.2015.10.080>
Reference: CEJ 14356

To appear in: *Chemical Engineering Journal*

Received Date: 18 June 2015
Revised Date: 9 October 2015
Accepted Date: 26 October 2015

Please cite this article as: Y. Chen, B. Lin, H. Wang, Y. Yang, H. Zhu, W. Yu, J-m. Basset, Surface modification of g-C₃N₄ by hydrazine: Simple way for noble-metal free hydrogen evolution catalysts, *Chemical Engineering Journal* (2015), doi: <http://dx.doi.org/10.1016/j.cej.2015.10.080>

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**Surface modification of g-C₃N₄ by hydrazine: Simple way for
noble-metal free hydrogen evolution catalysts**

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Abstract

The graphitic carbon nitride (g-C₃N₄) usually is thought to be an inert material and it's difficult to have the surface terminated NH₂ groups functionalized. By modifying the g-C₃N₄ surface with hydrazine, the diazanyl group was successfully introduced onto the g-C₃N₄ surface, which allows the introduction with many other function groups. Here we illustrated that by reaction of surface hydrazine group modified g-C₃N₄ with CS₂ under basic condition, a water electrolysis active group C(=S)SNi can be implanted on the g-C₃N₄ surface, and leads to a noble metal free hydrogen evolution catalyst. This catalyst has 40% hydrogen evolution efficiency compare to the 3 wt% Pt photo precipitated g-C₃N₄, with only less than 0.2 wt% nickel.

Keywords: surface modification; g-C₃N₄; hydrazinolysis; photo-catalytic hydrogen evolution; noble metal free.

1. Introduction

The global population grows very fast since the last century, and put very big pressure on the energy supply and environment. To make a balance, solar energy turns to be the best solution, which is the most sustainable and abundant energy on this world, but not easy to use due to its low energy density, availability and difficult in storage.¹ The use of hydrogen can compensate these weaknesses as a clean energy vector.²⁻⁴ However, how to obtain hydrogen economically and environmental friendly is the most challenging part. Photo-catalytic hydrogen production from water with semiconductor catalysts can be the best solution since it includes both advantage.⁵⁻⁷ Many pioneering works already have illustrated that inorganic semiconductor materials are suitable to split big water natural light for few decades ago.⁸⁻¹⁴ However, most of the catalysts contain big amount of poisonous or noble transition metals, which hinder their real application for economic and environmental reasons.¹⁵⁻¹⁸

Recently, due to the pioneering job of Wang,¹⁹ a polymeric carbon nitride material, reported by Liebig in the first time at 1834,²⁰ has attracted much attention for its application in the photo-catalytic hydrogen evolution. This material can be synthesized easily from cheap starting material, and is nontoxic, sustainable and environmental friendly. Due to the strong C-N good chemical stability and thermal stability (up to 600 °C). All these merits make it to be an idea material for the application in hydrogen evolution^{19,21-30} as well as environmental pollutant degradation.³¹⁻⁴⁰ g-C₃N₄ is a semiconductor with a band gap of 2.7 eV, with a VB level suitable for hydrogen and oxygen evolution both. But g-C₃N₄ itself has negligible activity in hydrogen evolution without co-catalyst, a rate only around 1 μmolh⁻¹ was found. Precious metal Pt (3% wt) always is photo-precipitated on g-C₃N₄ as a co-catalyst to achieve an applicable

hydrogen evolution rate, but the use of large quantity of noble metal Pt keeps this catalyst away from large scale application from the real situation consideration.²¹⁻³⁰

To make g-C₃N₄ an economic and applicable catalyst, people have made lots of efforts to decrease the cost for this catalyst, either by increasing the efficiency of the catalyst or avoiding the use of noble metals. Such as by increasing the surface area of g-C₃N₄,⁴²⁻⁴⁵ or doping C₃N₄ with other building blocks, elements or sensitizer,⁴⁶⁻⁵⁷ the hydrogen evolution efficiency can be improved. In the meanwhile, MoS₂, NiS₂, Ni(OH)₂ can be used as the co-catalyst for g-C₃N₄ in hydrogen evolution in some cases,^{46,58-60} but with high weight overloading, as well as lower efficiency and stability.

Figure 1: Schematic reaction mechanism for g-C₃N₄ based photo-catalytic hydrogen evolution.

The mechanism of carbon nitride photo-catalyzed hydrogen evolution involves following steps (Figure 1), g-C₃N₄ absorbs a photon with energy equal or higher than the band gap and produces an electron, the photo-generated electron migrates to the surface, then is trapped by the Pt nanoparticles deposited on the surface, which can enhance the charge separation due to lower work function and act as hydrogen electrolysis active center.⁶¹ However, the heterogeneous catalyst gets the activity from scarce locations on the surface, it's difficult to understand how the active species Pt

nanoparticles interact with the $g\text{-C}_3\text{N}_4$,⁶² thus difficult to improve the catalysis performance of $g\text{-C}_3\text{N}_4$ with a reasonable structure activity relationship.

We know that $g\text{-C}_3\text{N}_4$ is constructed by repeated tri-s-triazine units, with NH_2 groups on the surface as terminations. With our long term experience in surface organometallic chemistry and organic synthesis,⁶³⁻⁶⁶ we realized the NH_2 groups are good sites for anchoring hydrogen evolution active center, which leads to the co-catalyst free and noble-metal free hydrogen evolution catalysts. Due to the photo-generated electrons can transfer to the hydrogen evolution active centers which bonded on the surface, enhanced catalytic efficiency may can be expected (Figure 2).

Because of the relative chemical inertness of the surface NH_2 groups, no successful such report can be find. Even there are very limited reports on the study of tri-s-triazine compounds, however, the NH_2 or NR_2 group on the tri-s-triazine ring can be easily replaced by NHNH_2 under the hydrazinolysis condition,⁶⁶⁻⁷⁰ which has much better reactivity in many different chemical reactions.

Figure 2: Proposed surface modified C_3N_4 photo-catalytic water splitting for hydrogen generation

In this work, we have modified the surface of $g\text{-C}_3\text{N}_4$ with hydrazine and successfully introduced the high reactivity NHNH_2 group (Scheme 1), which can be converted to

dithiocarbamate group easily after reaction with CS₂. Noble metal free hydrogen evolution catalyst can be obtained when the dithiocarbamate group coordinated to Ni²⁺.

2. Experimental

2.1 Preparation of compounds

All chemicals are purchased from Sigma-Aldrich and used without further purification,

Scheme 1: The preparation of g-C₃N₄-N(NHCS₂Ni)

2.1.1 Compound 1 g-C₃N₄-NHNH₂. g-C₃N₄ is synthesized with the reported procedure from melamine as the starting material (Surface area 10.4 m²/g). 1 g of as-synthesized g-C₃N₄ was added into a 50 ml round bottom flask, followed with 20 ml water and 4 ml hydrazine hydrate. The mixture was stirred at 80 °C for 40 min. The reaction was stopped, the solid material was collected by filtration, and washed with diluted HCl to remove the monomer produced in the reaction for three times, then with water until the filtration shows a neutral pH value, diazanyl group modified specie **1** g-C₃N₄-NHNH₂ was obtained after dry.

2.1.2 Compound 2 g-C₃N₄-NHNH(CS₂Na). **1** as prepared was suspended in 25 ml ethanol, 0.5 ml of 1 M NaOH was added into the suspension, then 1 ml CS₂ was added to the mixture slowly by a syringe, the mixture was stirred at 40 °C for 2 h. The solid was collected and wash with water. The dithiocarbamate derivative **2 g-C₃N₄-NHNH(CS₂Na)** was thus obtained.

2.1.3 Compound 3 g-C₃N₄-NHNH(CS₂Ni). **2** was mixed with NiCl₂•6H₂O (5 wt%) in methanol/water (2:1), the suspension was allowed to stir at room temperature for half hour to afford the compound **3**.

2.2 Characterization

2.2.1 General

Infrared spectra (reflection) were recorded on a Nicolet Magna 6700 FT spectrometer. UV spectra were recorded on a JASCO V-670 spectrometer. TEM images were recorded on a Titan G2 60-300 model. Elemental analyses were performed at the Mikro analytisches Labor Pascher in Germany. Solid state NMR spectra were recorded on Bruker Avance 400. All chemical shifts were measured relative to residual ¹H or ¹³C resonance in the deuterated solvents.

2.2.2 Solid State Nuclear Magnetic Resonance

One dimensional ¹H MAS and ¹³C CP-MAS solid state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 and 100 MHz resonance frequencies for ¹H, ¹³C respectively, with a conventional double resonance 4mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 14 and 10 KHz for ¹H, ¹³C spectra, respectively. NMR chemical shifts are reported with respect to TMS as an external reference. For CP/MAS ¹³C NMR, the following sequence was used: 90° pulse

on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally acquisition of the ^{13}C signal under high power proton decoupling. The delay between the scan was set to 5 s, to allow the complete relaxation of the ^1H nuclei and the number of scans was between 3,000-30,000 for carbon, and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

2.2.2 Evaluation of photocatalytic activities

The photocatalytic H_2 evolution test was conducted using a recirculating batch reactor unit and a top-irradiated photocatalytic reactor using a Xenon lamp (125 mW/cm^2) equipped with a 420 nm cut-off filter (photon distribution see Figure S4). The temperature of reactant solution was kept constant at room temperature by a flow of cooling water during the test. The hydrogen amount was collected and analyzed with an online Agilent gas chromatograph. For hydrogen amount characterization, 50 mg photocatalysts was dispersed in 50 ml aqueous solution containing 10% (v/v) triethanolamine as sacrifice reagent.

3. Results and discussion

3.1 Screening of modification reaction conditions

To make the $\text{g-C}_3\text{N}_4$ surface modified with hydrazine group, we have carefully studied the reaction of $\text{g-C}_3\text{N}_4$ with hydrazine hydrate (Table 1). The $\text{g-C}_3\text{N}_4$ polymer is not very stable with hydrazine hydrate under severe reaction condition. In the sealed tube, $\text{g-C}_3\text{N}_4$ totally decomposed even after reaction with 10% hydrazine hydrate at 100°C for 4h, IR spectra show the future absorption band of $\text{g-C}_3\text{N}_4$ totally disappeared, strong absorption band can be found in the $3500\text{-}2700 \text{ cm}^{-1}$ region, which can be

assigned to heptazine 69-70(Figure S1), which indicated that the g-C₃N₄ has been decomposed.

By using IR as the characterization method, we can easily found out the decomposition of the compound in the reaction, and we can optimize the reaction conditions to make the g-C₃N₄ surface modified with hydrazine group.

g-C₃N₄ partially decomposed after reaction with 10% hydrazine hydrate at 100 °C for 6h, while no significant decomposition was observed when the reaction was performed at 80 °C for 2h. The monomer produced in the reaction can be washed away by diluted hydrogen chloride acid, after neutralizing the washing filtration, the monomer heptazine can be precipitated, which calculated to be around 1 wt% of the starting g-C₃N₄ after reaction with 5% hydrazine hydrate at 80 °C for 40min. And we use this condition as the standard condition for the surface modification of the g-C₃N₄.

Table 1: The surface modification reaction of the g-C₃N₄ with hydrazine

Reaction Condition	Reagent	Result
Sealed Tube 130 °C, 4h	NH ₂ NH ₂ •H ₂ O: H ₂ O =1:1	Decomposed
Sealed Tube 130 °C, 4h	NH ₂ NH ₂ •H ₂ O: H ₂ O =1:9	Decomposed
Sealed Tube 100 °C, 4h	NH ₂ NH ₂ •H ₂ O : H ₂ O=1:9	Decomposed
100 °C, open flask, 6h	NH ₂ NH ₂ •H ₂ O : H ₂ O=1:9	Partially decomposed
100 °C, open flask, 2h	NH ₂ NH ₂ •H ₂ O : H ₂ O=1:9	Partially decomposed
80 °C, open flask, 2h	NH ₂ NH ₂ •H ₂ O : H ₂ O=1:9	Not decomposed
80 °C, open flask, 40min	NH ₂ NH ₂ •H ₂ O : H ₂ O=1:19	Not decomposed

3.2 Characterization of surface modified species

IR, UV and XRD spectra didn't show significant difference between the raw $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4\text{-NHNH}_2$, but Solid-state (SS)-NMR can show the difference (see part 3.3, figure 5). We have tested the photo-catalysis activity of the surface hydrazine group modified $\text{g-C}_3\text{N}_4$. As the raw $\text{g-C}_3\text{N}_4$, no significant catalysis activity was observed with the modified $\text{g-C}_3\text{N}_4\text{-NHNH}_2$ itself, only after addition of Pt as the co-catalyst, hydrogen evolution can be observed, with a slightly lower rate than the raw $\text{g-C}_3\text{N}_4$ (Figure 3), but also has very good stability, no reaction rate decrease was found after 72 hours.

Figure 3: Time course of H_2 production from water containing 10 vol% triethanolamine as an electron donor under visible light (of wavelength longer than 420 nm) by (a) unmodified $\text{g-C}_3\text{N}_4$ with 3 wt% Pt (photodeposition) and (b) surface modified $\text{g-C}_3\text{N}_4\text{-NHNH}_2$ with 3 wt% Pt (photodeposition). (50 mg cat.; Xe lamp 125 mW/cm^2 ; 10 vol% triethanolamine aqueous solution, 50 mL).

3.3 Characterization of surface modified species

Powder XRD spectra show there is no difference between the XRD pattern of **3** and the precursor $\text{g-C}_3\text{N}_4$ (Figure 4). IR spectra also didn't detect significant difference between **3** and raw $\text{g-C}_3\text{N}_4$ (Figure S2), except for the IR band around 3200 cm^{-1} increased due to the NHNH_2 group. Uv-Vis spectrum identified the band gap of $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Ni})$ to be $2.7\text{ \AA}$ (Figure S3).

Figure 4: Powder-XRD of $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4(\text{NHNHCS}_2\text{Ni})$.

Figure 5: TEM images of (left) raw $\text{g-C}_3\text{N}_4$, (right) $\text{g-C}_3\text{N}_4$ (NHNHCS₂Ni). The left figure shows the TEM image of the unmodified $\text{g-C}_3\text{N}_4$. To make sure there is no Ni(OH)_2 or NiS nano-particles on the surface of C_3N_4 , which can act as co-catalysts for $\text{g-C}_3\text{N}_4$ in hydrogen evolution.

TEM experiments show that the surface of $\text{g-C}_3\text{N}_4$ remains homogeneous after the reactions and no nano-particle can be found (Figure 5), and confirms that neither NiS nor Ni(OH)_2 produced on the surface.

These results indicate the structure of $\text{g-C}_3\text{N}_4$ didn't change after three steps reaction (In the comparative experiment, $\text{g-C}_3\text{N}_4$ reacts with hydrazine hydrate under 120 °C for 2 h, $\text{g-C}_3\text{N}_4$ was found totally decomposed). Elemental analysis found $0.19 \pm 0.1\%$ S for **2** and $0.16 \pm 0.1\%$ S, $0.11 \pm 0.02\%$ Ni for **3**, with a Ni/S ratio around 1:3-4.

To identify the structure of the surface species, we characterized the product of each step by Solid-State (SS) NMR. For the raw $\text{g-C}_3\text{N}_4$, ^1H MAS (magic angle spinning) NMR shows a peak around 9.0 ppm, which can be assigned to NH_2 and NH groups; ^{13}C CP(cross polarization) MAS NMR shows two peaks at 164 ppm and 155 ppm. After reaction with hydrazine, ^{13}C CP-MAS NMR doesn't show any difference between $\text{g-C}_3\text{N}_4$ and **1**, but ^1H MAS NMR shows one new peak appears at 4.2 ppm (Figure 6a),

which attributes to NHNH_2 of the diazanyl group. That was confirmed by the treatment with NaNO_2 . It is known that diazanyl group reacts with NaNO_2 to produce triazo group, we found the peak at 4.2 ppm for **1** disappeared after reaction with excessive NaNO_2 at room temperature in ethanol for 15 min (Figure 6c). While in the reaction with CS_2 , the intensity of the peak for the NHNH_2 group decreased a lot (Figure 6b), indicating most of the diazanyl groups have been consumed in the preparation of **2**.

Figure 6: (a) ^1H MAS NMR of raw $\text{g-C}_3\text{N}_4$. (b) ^1H MAS NMR of $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Na})$. (c) ^1H MAS NMR of $\text{g-C}_3\text{N}_4\text{-N}_3$.

Figure 7: (a) ^{13}C CP-MAS NMR of raw $\text{g-C}_3\text{N}_4$. (b) ^{13}C CP-MAS NMR of $\text{g-C}_3\text{N}_4\text{-NHNH(CS}_2\text{Ni)}$.

For a better resolution of the ^{13}C NMR, ^{13}C enriched CS_2 (^{13}C 99%) was used to prepare ^{13}C labeled **2**. new peak appears at 219 ppm in ^{13}C CP-MAS NMR spectrum after **1** reacts with CS_2 (Figure 7b), which locates in the chemical shift region of dithiocarbamate derivatives and can be assigned to the carbon of (C=S)S group. Due to the very low concentration of the surface species, the signal for the carbon is still a little bit weak even after 50,000 scans.

The hydrogen evolution experiments were carried out with **3** in powder form with the reported condition. **3** was suspended in the water to perform the reaction. The as-prepared $\text{g-C}_3\text{N}_4\text{-NHNH(CS}_2\text{Ni)}$ achieved steady H_2 production from water with 10 vol% triethanolamine⁶ as a sacrificial reagent on light illumination (wave length > 420 nm).

A typical time course of hydrogen evolution from water using 3 wt% Pt deposited $\text{g-C}_3\text{N}_4$ is shown in Figure 8, curve (a). And the time course of hydrogen evolution with **3**

is shown in Figure 8, curve (b), which shows $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Ni})$ can work as a stable photo-catalyst for visible-light-driven H_2 production. By comparison we can found $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Ni})$ reaches 40% of the Pt deposited $\text{g-C}_3\text{N}_4$ hydrogen evolution rate. The evolution rate of H_2 with **3** is $3.7 \mu\text{mol/h}$, meanwhile the value for 3 wt% Pt-deposited $\text{g-C}_3\text{N}_4$ is $8.1 \mu\text{mol/h}$. If take the overloading of the metal used into account, $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Ni})$ has much higher catalysis efficiency compare to the 3 wt% Pt deposited $\text{g-C}_3\text{N}_4$. The reaction was allowed to proceed for a total of 16 h under visible-light irradiation, continuous H_2 evolution was observed with no noticeable change in the production rate and no noticeable degradation of the carbon nitride, which identified that the catalyst has quite good stability. The calculated quantum yield of this catalyst at 420 nm is around 1.4%.

Figure 8: A typical time course of H_2 production from water containing 10 vol% triethanolamine as an electron donor under visible light (of wavelength longer than 420 nm) by (a) unmodified $\text{g-C}_3\text{N}_4$ with 3 wt% Pt (photodeposition) and (b) only surface modified carbon nitride $\text{g-C}_3\text{N}_4\text{-NHNH}(\text{CS}_2\text{Ni})$. (50 mg cat.; Xe lamp 125 mW/cm^2 ; 10 vol% triethanolamine aqueous solution, 50 mL).

3.4 Catalytic stability and reactivity study of the surface modified species g-C₃N₄-NHNH(CS₂Ni)

Blank test was performed to make sure the hydrogen was produced by the surface bonded nickel. When NiCl₂ solution (3 wt% of g-C₃N₄) was directly added to a suspension of 50 mg g-C₃N₄ in 10 vol% triethanolamine, even with ultraviolet light (>300 nm), only negligible amount of H₂ was produced, which identified that the external Ni²⁺ can't help g-C₃N₄ to evolve hydrogen.

In the comparative experiments, NiS₂ or Ni(OH)₂ were deposited on g-C₃N₄ with the traditional method as the co-catalysts for the hydrogen evolution, the catalysts has very low reactivity with 0.2 wt% NiS₂ or Ni(OH)₂ co-catalyst overloading, when the NiS₂ or Ni(OH)₂ overloading increased to 3 wt%, only moderate reactivity was observed and lower than 3 wt% Pt photo-deposited g-C₃N₄. However, the stability of these catalysts are quite low, obvious reactivity decrease was observed even in the first 2 hours, and the color of the catalysts turned dark after the reaction begin for few hours.

In the previous reports, MoS₂, NiS and Ni(OH)₂ have been used as the co-catalysts for mpg-g-C₃N₄ (Table 2),⁵⁸⁻⁶⁰ which are the only few cases that g-C₃N₄ can catalyze the photo hydrogen evolution without noble metal. However, obvious reactivity decrease was observed even in the first 2 hours for all these catalysts, that is agree with what we found above.

While g-C₃N₄-NHNH(CS₂Ni) was used for the hydrogen evolution, except for the sacrifice triethanolamine, no any other additive is needed for the reaction. After 16 h photo hydrogen evolution reaction, no increase of the N₂ level was found, also no color change of the catalyst was observed. The reactivity of the catalyst didn't decrease after

three cycles (Figure S5). Compare to the NiS and Ni(OH)₂ co-catalyst, g-C₃N₄-NHNH(CS₂Ni) is quite stable in the hydrogen evolution reaction, in addition, take the >0.2% Ni overloading into account, much higher molecular catalysis efficiency has achieved.

We have compared our noble-metal free catalyst system with reported g-C₃N₄ hydrogen evolution systems (Table 2), usually noble-metal Pt was needed as the co-catalyst. Our catalyst system has a moderate reaction reactivity in all the catalysts based on the same kind of g-C₃N₄. In the few reported noble-metal free g-C₃N₄ hydrogen evolution cases, more efficient mpg-g-C₃N₄ was used, but much lower reactivity was found for co-catalysts Ni(OH)₂ and NiS compare to 3 wt% Pt, and the reactivity of the catalysts lost 30-50% after 16h.

Table 2: Rate of hydrogen production over a series of C₃N₄ catalysts together with the presence/absence of Pt, the sacrificial reagents used, light energy and light fluxes.

Reaction Condition	Pt(wt.%)	Rate mol _{gCatal} ⁻¹ h ⁻¹	Wavelength (nm)	Lamp power/Flux	Ref
g-C ₃ N ₄	3	140	>420	Xe 300W	19
g-C ₃ N ₄ (S-Dope)	3	120	>420	Xe 200W/0.8mWcm ⁻²	71
g-C ₃ N ₄ /Cu ₂ O	3	241	>420	Xe 300W/not given	72
g-C ₃ N ₄ /MoS ₂	1	230	>400	Xe 300W/not given QY=2.8% undefined	73
g-C ₃ N ₄ /Zn	0.5	60	>420	Xe 200W/0.8mWcm ⁻² QY=3.2% (420nm)	74
mpg-g-C ₃ N ₄	3	1490	>420	Xe 300W	42
mpg-g-C ₃ N ₄ /MoS ₂	0	Decrease quickly (1090)	>400	Xe 300W 4.7mWcm ⁻² QY=2.1% (420nm)	58

mpg-g-C ₃ N ₄ /Ni(OH) ₂	0	Decrease quickly (140)	>400	Xe 350W	59
mpg-g-C ₃ N ₄ /NiS	0	Decrease quickly (480)	>420	Xe 300W	60
g-C ₃ N ₄ (NH NHCS ₂ Ni)	0	70 ^g	>420	Xe 300W/57mWcm ⁻²	This work

BET surface area for mpg-g-C₃N₄= 70 m²/g. BET surface area for g-C₃N₄= 10 m²/g.

3. Conclusions

In conclusion, we developed a very simple way to active the inert surface of g-C₃N₄. By treatment with hydrazine, we introduced the diazanyl group to g-C₃N₄, it is capable to connect many different function groups or ligands. We illustrated that the modified g-C₃N₄ is a very good precursor for noble-metal free hydrogen evolution catalyst. After reaction with CS₂, dithiocarbamate ligand can be introduced easily onto the surface of g-C₃N₄, and leads to hydrogen evolution active species upon coordinating to Ni²⁺ (less than 0.2% nickel overloading). This catalyst reaches 40% activity of 3 wt% platinum deposited g-C₃N₄ in hydrogen evolution, and has a 1.4% QY under 420 nm irradiation. These results identified that the molecular level catalyst design strategy works well for the g-C₃N₄ based hydrogen evolution, the surface catalysis active molecule can effectively replace the traditional co-catalyst nanoparticle, and higher molecular catalysis efficiency was achieved. That represents a new way for the development of cheap and easy g-C₃N₄ hydrogen evolution catalysts.

Acknowledgements

We thank King Abdullah University of Science and Technology for the generous research support. YC thanks the support from Central South University. YY thanks the

support from Chinese Natural Science Foundation on contract No. 51102107, Zhejiang NSF (Grant LY12B02021) and “521” talent program of ZSTU.

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Surface modification of g-C₃N₄ with Hydrazine allows the easy introduction of other function groups.

General method for noble-metal free hydrogen evolution g-C₃N₄ catalyst with stable hydrogen evolution

0.2 wt% nickel on the modified g-C₃N₄ achieves 40% hydrogen evolution efficiency of 3 wt% Pt deposited g-C₃N₄