This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Ag$_2$O Modified g-C$_3$N$_4$ for Highly Efficient Photocatalytic Hydrogen Generation under Visible Light Irradiation

Ming Wu, Jun-Min Yan*, Xue-Wei Zhang, Ming Zhao, and Qing Jiang

The Ag$_2$O modified g-C$_3$N$_4$ (Ag$_2$O/g-C$_3$N$_4$) is synthesized by a facial hydrothermal reaction. The as-prepared Ag$_2$O/g-C$_3$N$_4$ shows the efficient photocatalytic property on hydrogen evolution by water splitting under visible light irradiation, which is about 274 times higher than that of pure g-C$_3$N$_4$, and is even much better than that of Pt/g-C$_3$N$_4$. More importantly, Ag$_2$O/g-C$_3$N$_4$ also demonstrates a relatively good recycling stability for photocatalytic hydrogen evolution.

1. Introduction

Photocatalysts for chemical conversion of solar energy have been vigorously pursued since the discovery of photolysis of water into hydrogen (H$_2$) and oxygen (O$_2$),$^1$ which has been recognized as a potential answer to the global energy crisis and environmental pollution.$^2$ An ideal photocatalyst should possess an appropriate band edge position for overall water splitting into H$_2$ or O$_2$ and a relative narrow band-gap for efficient utilization of visible light.$^3$ To date, numerous metal-based inorganic photocatalysts have been explored for water decomposition, such as metal-oxides,$^4$ metal-(oxy)sulfides,$^5$ and metal-(oxy)nitrides.$^{12,14}$ However, most of them are moderately active only in the ultraviolet region, and are still plagued by low thermal and chemical stabilities. Therefore, developing the new photocatalysts for water splitting with high activity and good stability under visible light is highly desirable but remained as a big challenge.

Recently, polymeric graphitic carbon nitride (g-C$_3$N$_4$) with a narrow band-gap of about 2.7 eV has been proposed as a promising “metal-free” photocatalyst for H$_2$ or O$_2$ production via water splitting under visible light irradiation.$^{15}$ g-C$_3$N$_4$ is constructed by tri-s-triazine units,$^{16,18}$ and the strong covalent bonds between carbon (C) and nitrogen (N) atoms can lead to the high stability of g-C$_3$N$_4$ in aqueous solutions ranging from acid to alkali.$^{19}$ Furthermore, g-C$_3$N$_4$ is environment benign and inexpensive relative to the metal-based photocatalysts.$^{20,21}$ All the above advantages endows g-C$_3$N$_4$ as a promising candidate for photocatalysis-driven application.$^{15}$ However, the pristine g-C$_3$N$_4$ always shows very low activity due to the rapid recombination rate of photo-generated charge carriers.$^{22,23}$ To improve its photocatalytic efficiency, several methods have been employed, for example, by doping with metal or nonmetal species, such as Au,$^{24}$ Fe,$^{25}$ K,$^{22,27}$ S,$^{28}$ B,$^{29}$ P,$^{30,31}$ I$^-$,$^{12}$ and C,$^{33}$ coupling with some other semiconductors$,^{34-37}$ synthesizing mesoporous structures or nanorods,$^{38-40}$ and sensitizing by organic dyes.$^{41}$

Although significant progress has been achieved, further increase of the activity of g-C$_3$N$_4$ to promote the kinetic property of H$_2$ generation from water splitting is still urgently needed. Ag$_2$O as a promising visible-light photocatalyst for the narrow band gap of 1.2 eV, has always been used to dope with other semiconductors.$^{42-47}$ However, there is no research on the photocatalytic hydrogen evolution by Ag$_2$O/g-C$_3$N$_4$ from water splitting.

In this work, by using a facile solvothermal method, Ag$_2$O/g-C$_3$N$_4$ composite has been successfully synthesized. The obtained composite demonstrates significantly enhanced photocatalytic activity for H$_2$ production than those of the pristine g-C$_3$N$_4$ and Pt/ g-C$_3$N$_4$ in the triethanolamine solution under visible-light irradiation. Moreover, the present photocatalyst also shows a good stability during the recycling application.

2. Experimental

2.1 Chemicals

Melamine (C$_6$H$_6$N$_6$, Aladdin Chemistry, ≥99%), Silver nitrate (AgNO$_3$, Beijing Chemicals Works, ≥99.8%), potassium phosphate monobasic (K$_3$HPO$_4$, 3H$_2$O, Sinopharm Chemical Reagent Co., Ltd, ≥99.8%), chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, Sinopharm Chemical Reagent Co., Ltd, ≥37% Pt basis), triethanolamine ((HOCH$_2$CH$_2$)$_3$N, Aladdin Chemistry, Reagent Co., Ltd, ≥99%) were used without any purification. Ultrapure water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

2.2 Preparation of Ag$_2$O/g-C$_3$N$_4$

The g-C$_3$N$_4$ powder was prepared by heating C$_3$H$_6$N$_6$ at 550°C for 4 h with a ramp rate of 4 °C min$^{-1}$ under N$_2$ atmosphere,$^{15}$ and the obtained sample was ground into powder in a mortar. And then, Ag$_2$O/g-C$_3$N$_4$ (weight ratio of Ag$_2$O/g-C$_3$N$_4$ is 0.83 wt %) was prepared by a facial hydrothermal
reaction method as follows: g-C3N4 (500 mg) and AgNO3 (6.1 mg, 0.036 mmol) were dispersed into 40 mL of water with sonication for 1 h. After that, K2HPO4 aqueous solution (0.1 mL, 0.18 mol L⁻¹) was added into the above solution at room temperature with magnetic stirring for 30 min. This obtained Ag3PO4/g-C3N4 suspension was placed in a Teflon-sealed autoclave (50 mL) and maintained at 160°C for 12 h. After natural cooling, the as-prepared sample was washed with water by 3 times. Finally, the washed specimen was dried at 60°C for 12 h. Samples with other different weight ratios of Ag2O/g-C3N4 (0.08 wt %, 0.42 wt %, 2.10 wt %, 4.20 wt %) have been prepared by the same method mentioned above.

2.3 Photocatalytic test

Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system. Hydrogen production was performed by dispersing 100 mg of the as-prepared catalyst in aqueous solution containing (HOCH2CH2)3N (100 mL, 10 vol. %) as a sacrificial electron donor. For Pt/g-C3N4 sample, 0.83 wt% of Pt was loaded on the surface of g-C3N4 through the in situ photodeposition method15 by using H2PtCl6 as the Pt precursor. The reaction solution was evacuated to remove air completely prior to the irradiation of the 300 W xenon-lamp (CEL-HXF 300, 320 < λ < 2500 nm) with a 420 nm cutoff filter (AULIGHT). The temperature of the reaction solution was maintained below 10°C by a flow of cooling water during the reaction. The evolved gas was analyzed by gas chromatography (GC7900) equipped with a thermal conductive detector (TCD), using N2 as the carrier gas.

2.4 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500pc X-ray diffractometer with Cu Kα irradiation (λ = 1.5406 Å) by a scan rate of 2°/min. Transmission electron microscope (TEM) together with an energy-dispersive X-ray spectroscopy (EDS) was operated by JEOI JEM-2010 microscope (accelerating voltage = 200 kV). X-ray photoelectron spectroscopy (XPS) results were obtained by an ESCALABMk II (Vacuum Generators) spectrometer using 300 W Al Kα radiation. All binding energies were referenced to C 1s peak at 284.6 eV of the surface adventitious carbon. Fourier transform infrared spectra (FTIR) of the samples were tested on a NEXUS-670 spectrometer at the room temperature. Ultraviolet-Visible (UV-Vis) diffuse reflection spectra were recorded on a UV-3600 spectrophotometer. The photoluminescence (PL) spectra were detected on a Hitachi F-7000 fluorescence spectrophotometer.

3. Results and discussion

Fig. 1a and b show the TEM images of the pure g-C3N4 and Ag2O/g-C3N4, respectively. From the XRD patterns of g-C3N4 and Ag2O/g-C3N4 (Fig. 1c), it can be seen that the two specimens show the similar main peaks at 2θ of 27.5° and 12.8°, corresponding to the interlayer16, 48 and in-plane structures19, 22 of g-C3N4, respectively. No Ag or its related oxide has been found for Ag2O/g-C3N4, which may be resulted from the low addition of Ag2O. However, the existence of Ag2O has been proved by the energy-dispersive X-ray spectroscopy (EDS) and high resolution XPS spectrum of Ag2O/g-C3N4 (Figs. 1d, and 2a). From the EDS results, elements of Ag, C, N, O, Cu and Si can be found in Ag2O/g-C3N4 (the existences of Cu and Si are attributed to the Cu grid and EDX detector, respectively). And from the Ag 3d X-
-PS analysis, two peaks at 368.0 and 374.0 eV related to phase of Ag2O can be found.45 Additionally, no element of P has been detected by EDS and XPS analyses (Figs. 1d, and 2b). Besides, the high resolution XPS spectra of C 1s and N 1s of Ag2O/g-C3N4 and pure g-C3N4 have been detected for comparison (Fig. 2c, d), where no obvious binding energy shift has been found between these two specimens, and all the peaks demonstrate the typical chemical states of C 1s and N 1s of g-C3N4.22 This means that the structure of g-C3N4 has not been changed or destroyed by Ag2O addition, which is consistent with the follow FTIR analysis (Fig. 3).

As shown in Fig. 3, the chemical structure of g-C3N4 and Ag2O/g-C3N4 are further investigated by FTIR analysis. For g-C3N4, there are three main absorption regions. The broad band peak loaded at 3000-3500 cm-1 is ascribed to the stretching vibration of N-H and O-H of physically adsorbed water.44 The absorption peak in 1200-1700 cm-1 is attributed to the typical breathing vibration of CN heteocycles, while the sharp peak at 809 cm-1 is attributed to the stretching vibration of triazine unites.16, 19 And all the three main absorption regions of Ag2O/g-C3N4 have no peak shift relative to pure g-C3N4, which agrees very well with the XPS result (Fig. 2c, d).

![FTIR spectra of pure g-C3N4 and Ag2O/g-C3N4.](http://example.com/ftir.png)

**Fig. 3** FTIR spectra of pure g-C3N4 and Ag2O/g-C3N4.

![UV-Vis diffuse reflectance spectra of g-C3N4 and Ag2O/g-C3N4.](http://example.com/uvvis.png)

**Fig. 4** (a) UV-Vis diffuse reflectance spectra of g-C3N4 and Ag2O/g-C3N4, (b) PL spectra of g-C3N4 and Ag2O/g-C3N4 with 370 nm excitation.

![Hydrogen evolution rate over pure g-C3N4 and Ag2O/g-C3N4.](http://example.com/hydrogen.png)

**Fig. 5** (a) Hydrogen evolution rate over pure g-C3N4 and Ag2O/g-C3N4 with different weight ratios of Ag2O/g-C3N4 under visible light irradiation within 4 h, (b) time course of hydrogen evolution over pure g-C3N4, Ag2O/g-C3N4 (Ag2O:g-C3N4=0.83 wt%) and Pt/g-C3N4 (Pt:g-C3N4=0.83 wt%) under visible light irradiation, and (b inset) time course of hydrogen evolution over pure g-C3N4 and Ag2O/g-C3N4 under simulated sunlight irradiation.

To investigate the electronic band structures, UV-Vis diffuse reflectance and PL spectra have been applied on the Ag2O/g-C3N4 and pure g-C3N4 for comparison. As shown in Fig. 4a, the UV-Vis adsorption of Ag2O/g-C3N4 has almost no red or blue shift compared with the pure g-C3N4, while its absorption intensity is higher than that of g-C3N4, indicating the higher utilization of the UV-Vis light. Fig. 4b shows the PL spectra of Ag2O/g-C3N4 and pure g-C3N4 (as a reference) excited by 370 nm at room temperature. The pure g-C3N4 has an emission peak at around 440 nm corresponding to its band gap of about 2.82 eV. Ag2O/g-C3N4 has much lower emission peak compared with the pure g-C3N4, which can be considered that the addition of Ag2O can effectively hinders the recombination rate of photogenerated electron–hole pairs,48-50 and thus may benefit for photocatalytic activity of Ag2O/g-C3N4 (vide infra).

Photocatalytic hydrogen evolution of the samples is evaluated under the visible light irradiation (λ>420 nm). As shown in Fig. 5a, Ag2O/g-C3N4 samples with different weight ratios of Ag2O: g-C3N4 show the great higher photocatalytic activities than the pure g-C3N4, and with the best catalyst of Ag2O/g-C3N4 (Ag2O:g-C3N4=0.83 wt%), hydrogen generation rate within 4 h can reach 33.04 μmol h-1, corresponding to 274 times higher than that of the pure g-C3N4 (0.12 μmol h-1). Further increase the Ag2O addition from 0.83 wt%, the activity of Ag2O/g-C3N4 decreases. This decrease may be caused by the shading effect,51-53 which can seriously hinder the absorption of incident light by g-C3N4 and decrease the surface active sites of g-C3N4. As shown in Fig. 5b, Ag2O/g-C3N4 (Ag2O:g-C3N4=0.83 wt%) can generate 132.14 μmol of hydrogen within 4 h, which is much better than pure g-C3N4 (0.49 μmol/h) and even Pt/g-C3N4 (43.30 μmol/h). Furthermore, under simulated sunlight irradiation without using the cutoff filter, Ag2O/g-C3N4 also shows excellent activity compared with g-C3N4 (Fig. 5b inset). It should be noted that pure Ag2O has no activity for hydrogen generation from water splitting due to its more
positive level of conduction band (CB) than redox potential of H'2/H2.

To test the stability of the synthesized catalysts, the recycling experiment with catalyst of Ag2O/g-C3N4 (Ag2O:Ag-C3N4=0.83 wt%) has been applied under visible light irradiation for 4 times with every period of 4 h (total reaction time is 16 h). As shown in Fig. 6, during the 4th run, 92.86 μmol hydrogen can be generated within 4 h. Although this value is slightly decreased compared with the 1st run (132.14 μmol/4 h), it is still higher than that of Pt/g-C3N4 (43.30 μmol/4 h, Fig. 5b).

To find the reason for the slight activity loss of Ag2O/g-C3N4, FTIR is analyzed on this catalyst after its 4th recycling application. With the results shown in Fig. 7a, it is found that the structure of g-C3N4 in Ag2O/g-C3N4 has no change or destruction after reaction. Therefore, the reduced reason might be caused by the change of Ag2O, and this can be confirmed by the XPS result in Fig. 7b, where Ag+ is partially reduced to be Ag0 after the recycling experiment. This change in the chemical state of Ag may be resulted from the photo-reduction during the photocatalytic reaction.

Based on the above analyses, the photocatalytic mechanism of Ag2O/g-C3N4 can be explained as Fig. 8. The bottom of conduction band (CB) for g-C3N4 (-1.12 eV, vs SHE) is more negative than that of Ag2O (0.20 eV, vs SHE), and the top of valence band (VB) for g-C3N4 (1.7 eV, vs SHE) is more positive than that of Ag2O (1.40 eV, vs SHE). Under visible light irradiation, the photogenerated holes of g-C3N4 can be transferred to the higher valance band (VB) of Ag2O. However, the photogenerated electrons of g-C3N4 cannot be transferred to conduction band (CB) of Ag2O because the redox potential of H'/H2 is higher than CB of Ag2O. And as the transferred holes are consumed, more photogenerated electrons could be used in photocatalytic hydrogen evolution, and thus enhance the catalytic activity.

Conclusions

In summary, we have successfully synthesized Ag2O/g-C3N4 by a facial hydrothermal reaction. Compared with the pure g-C3N4 and even Pt/g-C3N4, the photocatalytic hydrogen evolution rate of Ag2O/g-C3N4 under visible light irradiation has been greatly improved. Most importantly, even after 16 h of recycling experiment, Ag2O/g-C3N4 also shows much better photocatalytic activity than that of Pt/g-C3N4. The present easy synthetic method and effective Ag2O/g-C3N4 catalyst may provide a new idea for improving other photocatalysts in hydrogen evolution.

Acknowledgements

This work is supported in part by the National Natural Science Foundation of China (51471075, 51401084 and 51101070); National Key Basic Research, Development Program (2010CB631001).

Notes and references

Ag₂O/g-C₃N₄ shows high hydrogen evolution rate from water splitting, which is much more efficient than those of g-C₃N₄ and Pt/g-C₃N₄.