Polyoxometalates covalently combined with graphitic carbon nitride for photocatalytic hydrogen peroxide production†

Shen Zhao, Xu Zhao,*ab Shuxin Ouyangcde and Yongfa Zhuf

The polyoxometalate (POM) cluster [SiW11O39]8− (SiW11) with photoreductive ability has been successfully covalently combined with graphitic carbon nitride (g-C3N4) through an organic linker strategy. The hybrid catalyst g-C3N4–SiW11 exhibits efficient catalytic performance (15.2 μmol h−1) for photocatalytic H2O2 production in the presence of methanol and can stabilize the formed H2O2 under sunlight irradiation (AM 1.5 filter). The Koutecky–Levich plot obtained from electrochemical rotating disk electrode (RDE) analysis of the oxygen reduction reaction (ORR) for g-C3N4–SiW11 reveals that the value of electron transfer during the ORR process is 2.76. Combining the electron spin resonance (ESR), Koutecky–Levich plots, O2 temperature programmed desorption (O2−TPD) and density functional theory (DFT) calculation results, the enhanced O2 adsorption of g-C3N4–SiW11 can promote the two-electron reduction of O2 to H2O2.

Introduction

With increasing demands for a clean environment, green oxidant hydrogen peroxide (H2O2) is used as the terminal oxygen source in pulp bleaching, disinfection, and organic synthesis, producing H2O as the sole byproduct. Nowadays, many methods including the anthraquinone method, the direct synthesis from H2 and O2, the alcohol oxidation method and electrochemical syntheses have been adopted to produce H2O2. However, the above methods have two shortcomings: 1) large amounts of energy and organic solvents have been consumed and 2) organic impurities may contaminate the formed H2O2 and increase the difficulty of extraction. Therefore, an efficient, energy-saving and green method to produce H2O2 is highly desired.

\[
\begin{align*}
\text{R-CH2OH} + 2h^+ & \rightarrow \text{R-CHO} + 2H^+ \\
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 (0.68 \text{ V vs. NHE})
\end{align*}
\]

* Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China. E-mail: zhaoxu@rcees.ac.cn; Fax: +86 10 62849667; Tel: +86 10 62849667
a University of Chinese Academy of Sciences, Beijing, 100049, China
b TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, Tianjin, 300072, China
c Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China
d Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

Polyoxometalates (POMs) are composed of cations and polyanion clusters with structural diversity, in which the oxo-metal polyhedra of MOx (M = W, Mo, V, Nb, Ta; x = 5, 6) are the basic construction units. In the presence of light with abundant energy, the excitation of POMs refers to the charge transfer from O2− to M(x−1)2+ (x = 5, 6), leading to the formation of a hole center (O2−) and trapped electron center (M(x−1)+).
pair. The excited POMs can act as both electron donors and electron acceptors. In addition, the well-defined HOMO–LUMO band gaps of POMs inhibit the recombination of electrons and holes.\textsuperscript{7} Thus, POMs are capable of initiating hydrogen and oxygen evolution\textsuperscript{8a,b} carbon dioxide (CO\textsubscript{2}) reduction,\textsuperscript{9c} and selective organic synthesis\textsuperscript{8d} due to the strong photooxidative ability of the holes and photoreductive ability of the electrons. These advantages make POMs the ideal guest molecules for the g-C\textsubscript{3}N\textsubscript{4} host. However, the existing g-C\textsubscript{3}N\textsubscript{4}–POM hybrid catalysts based on weak interactions such as electrostatic interaction and metal–ligand coordination\textsuperscript{9} suffer from stability issues owing to POM leaching.\textsuperscript{10} The primary amine (–NH\textsubscript{2}) groups of g-C\textsubscript{3}N\textsubscript{4} frameworks can participate in organic reactions to introduce functional groups to g-C\textsubscript{3}N\textsubscript{4} frameworks.\textsuperscript{11} Though the POM cluster \([\text{PW}_{11}\text{O}_{39}]^{7−}\) (PW\textsubscript{11}) has been successfully covalently combined with three dimensionally ordered macroporous graphitic carbon nitride (3DOM g-C\textsubscript{3}N\textsubscript{4}) through an organic linker strategy for photocatalytic H\textsubscript{2}O\textsubscript{2} production,\textsuperscript{12} this catalytic system requires further improvement: 1) the amounts and reactivity of –NH\textsubscript{2} groups of g-C\textsubscript{3}N\textsubscript{4} need improvement to enhance the covalent interaction between g-C\textsubscript{3}N\textsubscript{4} and POMs; 2) the photoreductive ability of POMs needs improvement to promote the O\textsubscript{2} reduction under sunlight irradiation.

Herein, g-C\textsubscript{3}N\textsubscript{4} with larger amounts and higher reactivity of –NH\textsubscript{2} groups than 3DOM g-C\textsubscript{3}N\textsubscript{4} (Fig. S1A\textsuperscript{†}) has been prepared by thermally decomposing urea.\textsuperscript{13} The POM cluster [SiW\textsubscript{11}O\textsubscript{39}]\textsuperscript{7−} (SiW\textsubscript{11}) with more negative conduction band (CB) level than PW\textsubscript{11} (ref. 14) has been covalently combined with g-C\textsubscript{3}N\textsubscript{4} through an organic linker strategy (Fig. S2\textsuperscript{†}).\textsuperscript{15} The organosilicon agent (triethoxysilyl)-propyl isocyanate can act as the linker to covalently combine the SiW\textsubscript{11} cluster with g-C\textsubscript{3}N\textsubscript{4}. The hybrid catalyst g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11} with well-defined and stable structure can promote the two-electron reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} and stabilize the formed H\textsubscript{2}O\textsubscript{2} under sunlight irradiation (AM 1.5 filter). The experimental and density functional theory (DFT) calculation results reveal that the covalent combination of SiW\textsubscript{11} and g-C\textsubscript{3}N\textsubscript{4} can largely enhance the O\textsubscript{2} adsorption of SiW\textsubscript{11}, which can promote the two-electron reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}.

Results and discussion

The \textsuperscript{13}C MAS NMR spectra of g-C\textsubscript{3}N\textsubscript{4} (Fig. 1A) exhibit two typical signal groups of the g-C\textsubscript{3}N\textsubscript{4}; the first signal group at 163.1 and 165.2 ppm with a 1.9:1 intensity ratio is the resonances for the CN\textsubscript{2}(NH\textsubscript{2}) groups, and the second signal group at 156.9 ppm belongs to the CN\textsubscript{3} groups of the cyanamiduric nucleus.\textsuperscript{16} In contrast, the \textsuperscript{13}C MAS NMR spectra of g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11} (Fig. 1A) show not only the two typical signal groups of g-C\textsubscript{3}N\textsubscript{4} but also the signal group at 10.1 ppm assigned to the organosilicon linker. The presence of the signal at 10.1 ppm confirms that the organosilicon linker has been covalently linked with g-C\textsubscript{3}N\textsubscript{4}. The \textsuperscript{29}Si MAS NMR spectra of g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11} (Fig. 1B) display two resonance peaks centered at ~64.9 and ~85.2 ppm, which correspond to RSi(OM)\textsubscript{3} (T\textsuperscript{1} mode, R = CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}NH(C==O), M = Si or W) and the heteroatom of the SiW\textsubscript{11} cluster, respectively. The presence of the T\textsuperscript{3} signal reveals the three M–O–Si (M = Si or W) bonds around the Si atom, confirming that the organosilicon linker is covalently tethered onto the vacancy of the SiW\textsubscript{11} cluster.\textsuperscript{17} The above \textsuperscript{13}C and \textsuperscript{29}Si MAS NMR results confirm that the SiW\textsubscript{11} cluster has been successfully covalently combined with g-C\textsubscript{3}N\textsubscript{4} by the organosilicon linker.

The XRD pattern of g-C\textsubscript{3}N\textsubscript{4}, K-SiW\textsubscript{11} and g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11} is shown in Fig. S3.\textsuperscript{†} The diffraction peaks located at 13.1\textdegree, 27.6\textdegree of g-C\textsubscript{3}N\textsubscript{4} are assigned to g-C\textsubscript{3}N\textsubscript{4} with (100) and (002) lines, which come from in-plane repeating tri-s-triazine and stacking of the conjugated aromatic units, respectively.\textsuperscript{18} For g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11}, the weak intensity of characteristic peaks at 27.6\textdegree and the presence of typical SiW\textsubscript{11}-related peaks in the range of 8–11\textdegree indicate that the SiW\textsubscript{11} cluster has been successfully covalently combined with g-C\textsubscript{3}N\textsubscript{4} through the organosilicon linker.\textsuperscript{19,20} Fig. S4\textsuperscript{†} shows the IR spectra of g-C\textsubscript{3}N\textsubscript{4}, K-SiW\textsubscript{11} and g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11}. The peaks in the range of 1156–1741 cm\textsuperscript{−1} have been observed in both g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11}, which are the typical vibrations of heptazine-based molecular units.\textsuperscript{20} The vibrations at 1051, 957, and 883 cm\textsuperscript{−1} corresponding to the W=O, Si–O, and W–O–W chemical bonds in the Keggin-type POM SiW\textsubscript{11} can be found in both K-SiW\textsubscript{11} and g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11}.\textsuperscript{19} The above IR results

![Fig. 1](image_url) **Fig. 1** \textsuperscript{13}C (A) and \textsuperscript{29}Si (B) MAS NMR spectra of g-C\textsubscript{3}N\textsubscript{4}, K-SiW\textsubscript{11} and g-C\textsubscript{3}N\textsubscript{4}–SiW\textsubscript{11}.
indicate that the primary structure of g-C3N4 and the SiW11 cluster has been well preserved after covalent combination. In addition, the broad peaks at around 3100–3400 cm–1 are mainly due to the –NH2 groups of the adsorbed H2O from air, which become weaker after covalent combination,11 indicating the decreased content of surface –NH2 groups in g-C3N4–SiW11. CO2 temperature programmed desorption (CO2-TPD) has been performed to investigate the amount of –NH2 groups in g-C3N4 and g-C3N4–SiW11 as –NH2 groups can act as Lewis base sites and adsorb slightly acidic CO2 molecules.20 Fig. S5† shows that the peak area of g-C3N4–SiW11 is much smaller than that of g-C3N4. Furthermore, the zeta potentials of aqueous suspension of g-C3N4 and g-C3N4–SiW11 have been measured because the –NH2 groups with free lone pair electrons on nitrogen atoms can act as proton acceptors and acquire positive surface charges.21 Fig. S6† shows that the zeta potential of g-C3N4–SiW11 (–22.8 mV) is more negative than that of g-C3N4 (–14.9 mV). The above IR, CO2-TPD and zeta potential measurement results reveal the significant decrease in the amount of –NH2 groups in g-C3N4 after covalent combination, confirming the reaction between the –NH2 groups of g-C3N4 and the organosilicon linkers. The nitrogen adsorption–desorption isotherms and pore size distribution patterns for g-C3N4 and g-C3N4–SiW11 are shown in Fig. S7.† The isotherms for g-C3N4 and g-C3N4–SiW11 (Fig. S7A†) show a type IV isotherm with a type H3 hysteresis loop. These two catalysts present a broad pore-size distribution curve (1–94 nm) from a small mesopore centered at 3.8 nm to a large mesopore centered at 32.7 nm (Fig. S7B†). The above results confirm that both g-C3N4 and g-C3N4–SiW11 possess a clear mesoporous structure.9,10,22 The surface area, pore volume and pore diameter of g-C3N4 and g-C3N4–SiW11 are shown in Table S1.† Compared with g-C3N4, the increase in these values of g-C3N4–SiW11 is due to the exfoliation and tailoring of the sheet structure of g-C3N4 after covalent combination.11 Thermogravimetric analysis (TGA) curves for g-C3N4, K-SiW11 and g-C3N4–SiW11 are shown in Fig. S8.† The total weight loss of g-C3N4 is 97.21% between 30 and 800 °C due to the direct thermal decomposition of g-C3N4. For K-SiW11, the weight loss in the range of 30–160 °C (2.02%) corresponds to the loss of physisorbed water and crystallization water, and the weight loss in the range of 160–800 °C (2.55%) is assigned to the Keggin structure decomposition.17 According to the above results, the actual weight percentage of the SiW11 cluster for g-C3N4–SiW11 is 18.25%. Combining the TGA, EA and ICP analysis (Table S2†), the molecular formulas of g-C3N4 and g-C3N4–SiW11 can be given as C2.61N4H1.55 and C2.61N4H1.55(K4SiW11O42Si2C8H14N2)0.007 (18.25 wt% SiW11).

As shown in Fig. 2A, the XPS peaks of C 1s for g-C3N4 and g-C3N4–SiW11 can be fitted to two peaks at binding energies of around 283.8 and 287.1 eV, which are ascribed to the tertiary carbon C–N groups and the C–C groups, respectively.12,23 The area ratios of these two peaks are 0.19 and 0.45 for g-C3N4 and g-C3N4–SiW11. The large increase in the amount of C–C groups supports that the organosilicon linker has been covalent linked with g-C3N4. Nevertheless, the XPS peaks of N 1s (Fig. 2B) for g-C3N4 can be fitted to the three peaks at 397.6, 399.2, and 403.7 eV, which are assigned to N–(C2), N–(C3), and –NH2, respectively.12,23 However, g-C3N4–SiW11 only exhibits two peaks at 397.5 and 399.1 eV corresponding to N–(C2) and N–(C3). The disappearance of the –NH2 peak indicates that the –NH2 groups of g-C3N4 react with the NCO– groups of the silane coupling agent to form carbamido groups during the covalent combination of the SiW11 cluster with g-C3N4. The above C 1s and N 1s XPS results support the 13C MAS NMR results of g-C3N4 and g-C3N4–SiW11.

Fig. 2  C 1s (A), N 1s (B), Si 2p (C), W 4f (D), and O 1s (E) XPS spectra of g-C3N4, K-SiW11, and g-C3N4–SiW11.
SiW_{11}. Both g-C_{3}N_{4} and g-C_{3}N_{4}−SiW_{11} show one Si 2p XPS peak at 101.2 eV (Fig. 2C). In addition, the XPS peaks of W 4f (Fig. 2D) for K-SiW_{11} and g-C_{3}N_{4}−SiW_{11} can be fitted to two peaks at binding energies of around 34.5 and 36.6 eV (W 4f_{7/2} and W 4f_{5/2}), which are consistent with the W(VI) oxidation state. The Si 2p and W 4f XPS results reveal that the primary structure of the SiW_{11} cluster has been well preserved after covalent combination. The XPS peaks of O 1s (Fig. 2E) for K-SiW_{11} and g-C_{3}N_{4}−SiW_{11} can be fitted to two peaks at binding energies of around 531.3 and 529.8 eV, which are ascribed to W−O−W/Si and W=O, respectively. The area ratios of these two peaks are 0.12 and 3.51 for K-SiW_{11} and g-C_{3}N_{4}−SiW_{11}. The tremendous increase of the peak area of W−O−W/Si supports that the organosilicon linkers are covalently tethered onto the vacancy of the SiW_{11} cluster. The above XPS results confirm that the SiW_{11} cluster has been covalently combined with g-C_{3}N_{4} through the organosilicon linker and the primary structure of SiW_{11} cluster has been well preserved after covalent combination.

Fig. S9† shows the TEM images of g-C_{3}N_{4} (Fig. S9A−C†) and g-C_{3}N_{4}−SiW_{11} (Fig. S9D−F†), which exhibit a sheet-like structure. However, SiW_{11} clusters cannot be observed obviously in the HR-TEM images of g-C_{3}N_{4}−SiW_{11} (Fig. S9D−F†), mainly due to the SiW_{11} clusters being highly dispersed on g-C_{3}N_{4}. To investigate the dispersion of SiW_{11} on g-C_{3}N_{4}, STEM mapping characterization has been performed. As shown in Fig. S10A† g-C_{3}N_{4}−SiW_{11} retains its sheet-like structure after covalent combination. The STEM image in Fig. S10B† shows a rough defect-rich surface with curvatures, distortions, protuberances, and crumpled edges. The elemental mapping images of C, N, Si, W, and O (Fig. S10C−H†) clearly exhibit that the SiW_{11} clusters are highly dispersed on the surface of g-C_{3}N_{4} after covalent combination.

The above characterization results confirm that the SiW_{11} cluster has been covalently combined with g-C_{3}N_{4} to form the hybrid catalyst g-C_{3}N_{4}−SiW_{11}. Furthermore, the catalytic performance of g-C_{3}N_{4}−SiW_{11} should be investigated.

The photocatalytic H_{2}O_{2} production over various catalysts has been conducted and monitored under O_{2}-equilibrated conditions and sunlight irradiation (AM 1.5 filter) in the presence of 5 vol% methanol at 25 °C. As shown in Fig. 3A, H_{2}O_{2} can be rapidly generated over g-C_{3}N_{4}−SiW_{11} and the amounts of formed H_{2}O_{2} can reach 17.8 μmol in 60 minutes. The catalytic performance of individual g-C_{3}N_{4} (8.7 μmol in 60 minutes) or K-SiW_{11} (1.0 μmol in 60 minutes) is lower than that of g-C_{3}N_{4}−SiW_{11}. For comparison, g-C_{3}N_{4}−SiW_{11}-IMP based on the electrostatic interaction has been prepared through an impregnation method with the same SiW_{11} weight percentage.

\[ \text{Formed H}_2\text{O}_2 (\mu\text{mol}) \]

\[ \text{Time (min)} \]

\[ \text{None} \quad \text{K-SiW}_{11} \quad g-C_{3}N_{4} \quad g-C_{3}N_{4}−SiW_{11} \quad g-C_{3}N_{4}−SiW_{11}-IMP \]

\[ \text{Dark} \quad \text{Light} \]

\[ \text{Wavelength (nm)} \]

\[ \text{320} \quad \text{370} \quad \text{420} \quad \text{470} \quad \text{520} \]

\[ \text{Apparent Quantum Yield (%)} \]

\[ \text{25 °C} \]

\[ \text{O}_2\text{-equilibrated, AM 1.5 filter} \]

\[ \text{Catalysis Science & Technology} \]

\[ \text{Paper} \]

\[ \text{Published on 13 February 2018.} \]

\[ \text{View Article Online} \]

\[ \text{Published on 13 February 2018.} \]

\[ \text{Downloaded by Tsinghua University on 12/16/2019 3:14:03 PM.} \]
as g-C$_3$N$_4$-SiW$_{11}$ based on covalent interaction. g-C$_3$N$_4$-SiW$_{11}$-IMP shows lower catalytic performance (9.6 μmol in 60 minutes). The reaction cannot proceed in the absence of a catalyst (<0.1 μmol in 60 minutes). Table S3† shows that H$_2$O$_2$ can be produced with a high selectivity of 86.6% over g-C$_3$N$_4$ (ref. 4b and c), while the selectivity over K-SiW$_{11}$ is 3.0% during the 60 minute photoreaction. The above results reveal that the SiW$_{11}$ cluster is an efficient catalyst for methanol photooxidation while g-C$_3$N$_4$ can enhance the selectivity of H$_2$O$_2$. Though g-C$_3$N$_4$-SiW$_{11}$-IMP based on the electrostatic interaction can increase the H$_2$O$_2$ production (9.6 μmol in 60 minutes), it can’t maintain the high selectivity of H$_2$O$_2$ (22.2%). Only the g-C$_3$N$_4$-SiW$_{11}$ based on covalent interaction can both increase the H$_2$O$_2$ production (17.8 μmol in 60 minutes) and maintain the high selectivity of H$_2$O$_2$ (80.1%). As shown in Fig. S1B, g-C$_3$N$_4$ exhibits better catalytic performance for the photocatalytic H$_2$O$_2$ production than 3DOM g-C$_3$N$_4$ under sunlight irradiation (AM 1.5 filter) because g-C$_3$N$_4$ has larger amounts of –NH$_2$ groups than 3DOM g-C$_3$N$_4$ (Fig. S1A†). In addition, the effect of sacrificial agents (methanol, ethanol and i-propanol) has been investigated. The results in Fig. S11† reveal that the highest H$_2$O$_2$ production can be obtained using methanol as the sacrificial agent because methanol is the easiest to be oxidized. The photocatalytic H$_2$O$_2$ production over g-C$_3$N$_4$ and g-C$_3$N$_4$-SiW$_{11}$ has been performed under N$_2$- and O$_2$-equilibrated conditions to investigate the role of O$_2$ in the photocatalytic H$_2$O$_2$ production (Fig. S12†). Generally, the photoexcited CB electrons can be scavenged by dissolved O$_2$ under O$_2$-equilibrated conditions but the protons should take up the electrons in the absence of O$_2$ (N$_2$-equilibrated conditions). Under N$_2$-equilibrated conditions, no H$_2$O$_2$ can be formed over both g-C$_3$N$_4$ and g-C$_3$N$_4$-SiW$_{11}$, confirming that H$_2$O$_2$ is generated through the O$_2$ reduction. g-C$_3$N$_4$-SiW$_{11}$ exhibits efficient catalytic performance for the photocatalytic H$_2$O$_2$ production under sunlight irradiation (AM 1.5 filter). As the absorption maxima of the POM cluster were found in the ultraviolet (UV) region, the catalytic performance of g-C$_3$N$_4$ and g-C$_3$N$_4$-SiW$_{11}$ under visible light (λ ≥ 400 nm) have been investigated. Fig. S13† shows that both g-C$_3$N$_4$ and g-C$_3$N$_4$-SiW$_{11}$ exhibit lower catalytic performance under visible light (λ ≥ 400 nm) than those under sunlight irradiation (AM 1.5 filter). However, the catalytic performance of g-C$_3$N$_4$-SiW$_{11}$ is always better than that of g-C$_3$N$_4$, suggesting that the covalent combination of SiW$_{11}$ and g-C$_3$N$_4$ can promote the photocatalytic H$_2$O$_2$ production.

$$[\text{H}_2\text{O}_2] = \frac{K_3}{K_d} (1 - \exp(-d))$$ (5)

The formation and decomposition of H$_2$O$_2$ over catalysts proceed through two competitive pathways owing to the thermodynamic instability of H$_2$O$_2$ at room temperature. The $K_d$ and $K_e$ values have been estimated by substituting the data in Fig. 3A to eqn (5), and the results are presented in Table S4. In order to investigate the stability of different catalysts, the reaction time has been extended to 360 minutes. The maximum amounts of formed H$_2$O$_2$ over g-C$_3$N$_4$-SiW$_{11}$, g-C$_3$N$_4$-SiW$_{11}$-IMP, g-C$_3$N$_4$ and K-SiW$_{11}$ is obtained to be 91.4, 24.0, 19.1 and 3.7 μmol in 360 minutes, respectively (Fig. 3B), giving the H$_2$O$_2$ formation rate of 15.2, 4.0, 3.2 and 0.6 μmol h$^{-1}$ for g-C$_3$N$_4$-SiW$_{11}$, g-C$_3$N$_4$-SiW$_{11}$-IMP, g-C$_3$N$_4$ and K-SiW$_{11}$ (Table S4†). The values of $K_d$ obtained from the photocatalytic H$_2$O$_2$ production over different catalysts (Table S4†) decrease in the following order: g-C$_3$N$_4$-SiW$_{11}$ (0.4831 μmol min$^{-1}$) > g-C$_3$N$_4$-SiW$_{11}$-IMP (0.2981 μmol min$^{-1}$) > g-C$_3$N$_4$ (0.2862 μmol min$^{-1}$) > K-SiW$_{11}$ (0.0255 μmol min$^{-1}$) > none (0.0027 μmol min$^{-1}$), which is consistent with the above H$_2$O$_2$ formation rate over different catalysts (Table S4†). Furthermore, the values of $K_d$ obtained from the photocatalytic H$_2$O$_2$ decomposition over different catalysts (Fig. S14†) increase in the following order: none (0.0093 min$^{-1}$) < K-SiW$_{11}$ (0.0163 min$^{-1}$) < g-C$_3$N$_4$ (0.0183 min$^{-1}$) < g-C$_3$N$_4$-SiW$_{11}$ (0.0232 min$^{-1}$) < g-C$_3$N$_4$-SiW$_{11}$-IMP (0.0254 min$^{-1}$). The $^{29}$Si MAS NMR for used g-C$_3$N$_4$-SiW$_{11}$ (Fig. S15†) reveals no signal of the polyperoxometalate species of the SiW$_{11}$ cluster, which rules out the formation of polyperoxometalate species during the photocatalytic H$_2$O$_2$ production. The above results confirm that the covalent combination of SiW$_{11}$ and g-C$_3$N$_4$ can stabilize the formed H$_2$O$_2$ under sunlight irradiation (AM 1.5 filter). Above all, the covalent combination of SiW$_{11}$ and g-C$_3$N$_4$ can promote the two-electron reduction of O$_2$ to H$_2$O$_2$ and stabilize the formed H$_2$O$_2$ under sunlight irradiation (AM 1.5 filter).

Under similar reaction conditions over the g-C$_3$N$_4$-based catalysts with electron donors of alcohol, the H$_2$O$_2$ formation rate (15.2 μmol h$^{-1}$) over g-C$_3$N$_4$-SiW$_{11}$ is higher than those over g-C$_3$N$_4$ (2.5 μmol h$^{-1}$), meso-g-C$_3$N$_4$ (3.8 μmol h$^{-1}$), g-C$_3$N$_4$-KPO (10.0 μmol h$^{-1}$) and 3DOM g-C$_3$N$_4$-PW$_{11}$ (10.4 μmol h$^{-1}$, Fig. S16†). In addition, the catalytic performance of g-C$_3$N$_4$-SiW$_{11}$ (15.2 μmol h$^{-1}$) is higher than that of carbonate-surface modified bimodal size distribution-Au/TiO$_2$ (BM-Au/TiO$_2$-CO$_3$$_2$$_5$-, 10.0 μmol h$^{-1}$). The apparent quantum yields (AQYs) of photocatalytic H$_2$O$_2$ production have been compared between g-C$_3$N$_4$ and g-C$_3$N$_4$-SiW$_{11}$. Fig. 3C shows that the AQYs of g-C$_3$N$_4$-SiW$_{11}$ in the UV range are 29.2% at 320 nm and 22.8% at 370 nm. In the visible light region, the AQY at 420 nm was 6.5%, which is 3 times higher than that for g-C$_3$N$_4$ at 420 nm (Φ$_{420}$ = 1.9%). The AQY value at 320 nm for g-C$_3$N$_4$-SiW$_{11}$ (Φ$_{320}$ = 29.2%) is higher than those for g-C$_3$N$_4$ (Φ$_{320}$ = 21.5%) and g-C$_3$N$_4$-KPO (Φ$_{320}$ = 26.2%). Furthermore, the formed H$_2$O$_2$ can reach 1.8 μmol in 60 minutes over g-C$_3$N$_4$-SiW$_{11}$ without an electron donor (Fig. 3D), suggesting that g-C$_3$N$_4$-SiW$_{11}$ can act as a dual-functional catalyst for both water oxidation (Fig. S17†) and oxygen reduction. Therefore, the relatively high H$_2$O$_2$ formation rates among the reported g-C$_3$N$_4$-based catalysts and the ability to produce H$_2$O$_2$ without an electron donor make g-C$_3$N$_4$-SiW$_{11}$ a promising catalyst for photocatalytic H$_2$O$_2$ production.

Photoelectrochemical characterization should be performed to clarify the reason for the efficient activity of g-C$_3$N$_4$-SiW$_{11}$.
g-C₃N₄–SiW₁₁. As shown in Fig. S18A, the photocurrent density of g-C₃N₄–SiW₁₁ (0.45 μA cm⁻²) is much larger than that of g-C₃N₄ (0.13 μA cm⁻²). Photoelectrochemical impedance spectroscopy (PEIS) results are shown in Fig. S18B. The diameter of the Nyquist semicircle for g-C₃N₄–SiW₁₁ is smaller than that of g-C₃N₄, which indicates that the g-C₃N₄–SiW₁₁ composites have lower resistances than g-C₃N₄. The emission peak appearing at about 458 nm in photoluminescence (PL) spectra of g-C₃N₄ and g-C₃N₄–SiW₁₁ is attributed to the direct electron–hole recombination of band transition. Compared with g-C₃N₄, g-C₃N₄–SiW₁₁ exhibits a weaker emission peak (Fig. S19A†). The above results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can enhance the charge separation of g-C₃N₄–SiW₁₁.

Electron spin resonance (ESR) analysis with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin-trapping reagent has been performed to confirm the pathway of O₂ reduction over different catalysts. Fig. 4A shows the ESR spectra of the solutions recovered after photoreaction over g-C₃N₄ and g-C₃N₄–SiW₁₁ for 3 minutes. Both solutions exhibit distinctive signals assigned to the DMPO–˙OOH spin adduct (α₉ = 13.1 G, α₁₀ = 9.8 G, g = 2.0059).† The signal intensity for the solution obtained by photoreaction over g-C₃N₄–SiW₁₁ is much weaker than that over g-C₃N₄. In order to quantify the ˙OOH concentration, nitro blue tetrazolium (NBT) has been chosen as a ˙OOH radical scavenger because NBT can be reduced by ˙OOH radicals and formed purple formazan, which was insoluble in water.²³ Fig. S20† shows the evolution of NBT disappearance and the subsequent formation of ˙OOH radicals during the photocatalytic H₂O₂ production over g-C₃N₄ and g-C₃N₄–SiW₁₁. After the covalent combination of SiW₁₁ with g-C₃N₄, the amounts of ˙OOH radicals decrease significantly (Fig. S20B†). Scavenger experiments using p-benzoquinone (PBQ) have been performed to investigate the role of ˙OOH. As can be seen from Fig. S21† the addition of PBQ can actually depress the photocatalytic H₂O₂ production over g-C₃N₄, while the addition of PBQ has no effect on the photocatalytic H₂O₂ production over g-C₃N₄–SiW₁₁. The ESR signal and quantitative and ˙OOH scavenger experimental results suggest that one-electron reduction of O₂ (eqn (3)) is indeed suppressed over g-C₃N₄–SiW₁₁, which thus promotes the two-electron reduction of O₂ (eqn (2)).

Electrochemical rotating disk electrode (RDE) analysis of the oxygen reduction reaction (ORR) further investigates the pathway of O₂ reduction. Fig. S22† shows the LSV curves of g-C₃N₄, TBA-SiW₁₁ and g-C₃N₄–SiW₁₁ measured on the RDE in an O₂-saturated 0.1 M phosphate buffer solution (pH 7) at different rotating speeds. The lipophilic tetrabutyl ammonium (TBA) salt of SiW₁₁ was used because TBA–SiW₁₁ is insoluble in the above 0.1 M phosphate buffer solution.⁹α Fig. 4B summarizes the Koutecky–Levich plots of the data at −0.9 V vs. Ag/AgCl.²⁹ The n value for g-C₃N₄ (n = 1.68)
suggests that one-electron O₂ reduction indeed occurs, which confirms the ESR results. In contrast, the \( n \) value for TBA–SiW₁₁ (\( n = 3.67 \)) reveals that the SiW₁₁ cluster can promote the two-electron O₂ reduction reaction. Therefore, the covalent combination of the SiW₁₁ cluster with g-C₃N₄ can promote the two-electron O₂ reduction reaction. The energy levels. In addition, the HOMO–LUMO gap of g-C₃N₄–SiW₁₁ (3.55 eV) is obviously smaller than that of SiW₁₁–organic linker (4.07 eV). The electrons at both HOMO and LUMO+2 energy levels of the g-C₃N₄–SiW₁₁ model are mainly located at the oxygen atoms of the SiW₁₁ unit due to the high electron affinity of the SiW₁₁ unit, indicating that the SiW₁₁ unit can behave as both oxidation and reduction sites.

As shown in Table S7, the absolute value of the calculated total negative charge localized on O atoms in the SiW₁₁ cluster of g-C₃N₄–SiW₁₁ is 29.77 [e], which is lower than that of the SiW₁₁ cluster of SiW₁₁–organic linker (30.07 [e]). The covalent combination of SiW₁₁ and g-C₃N₄ results in the decrease in the surface charge of the SiW₁₁ cluster and increase in the adsorption capacity of O₂, which is consistent with the O₂–TPD results (Fig. 4C). The O₂–TPD results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can enhance the O₂ adsorption of SiW₁₁. Therefore, the experimental and DFT calculation results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can largely enhance the O₂ adsorption of SiW₁₁, which can promote the two-electron reduction of O₂ to H₂O₂.

The catalytic results reveal that g-C₃N₄–SiW₁₁ is truly heterogeneous for H₂O₂ production, and heterogeneous

![Fig 5](image-url)
g-C₃N₄–SiW₁₁ can be recycled five times under the same conditions (Fig. S24†). The characterization results reveal that the structure and composition of the used g-C₃N₄–SiW₁₁ remain unchanged (Fig. S15, S25, S26 and Table S2†). The above results indicate that the heterogeneous g-C₃N₄–SiW₁₁ is catalytically stable.

**Conclusions**

To summarize, to optimize the structure of g-C₃N₄–POMs, the g-C₃N₄ with larger amounts and higher reactivity of –NH₂ groups than 3DOM g-C₃N₄ has been prepared by thermally decomposing urea. The POM cluster of SiW₁₁ with more negative CB level than PW₁₁ has been covalently combined with g-C₃N₄ through an organic linker strategy. The organosilicon agent (triethoxysilyl)-propyl isocyanate can act as the linker to covalently combine the SiW₁₁ cluster with g-C₃N₄. The hybrid catalyst g-C₃N₄–SiW₁₁ exhibits efficient catalytic performance (15.2 μmol h⁻¹) for photocatalytic H₂O₂ production in the presence of methanol and can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter). Three reasons have been presented for the efficient catalytic performance of g-C₃N₄–SiW₁₁ from the catalytic and characterization results: 1) the conduction band (CB) level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) is more positive than that of the one-electron reduction of O₂ to 'OH (−0.13 V vs. NHE) and the potential difference between the CB level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) and the O₂ to H₂O₂ potential (0.69 V vs. NHE) is sufficient (0.78 V), which can promote the two-electron reduction of O₂ to H₂O₂; 2) the hybrid catalyst of g-C₃N₄–SiW₁₁ can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter); and 3) most importantly, the experimental and DFT calculation results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can largely enhance the O₂ adsorption of SiW₁₁, which can promote the two-electron reduction of O₂ to H₂O₂.

**Experimental section**

**Preparation of g-C₃N₄–SiW₁₁**

12 g-C₃N₄ (1.00 g) was dispersed in 50 ml isopropanol, and (triethoxysilyl)-propyl isocyanate (1.00 g, 4.04 mmol) was added. The reaction mixture was kept at 80 °C, to which small amounts of triethylamine were added. After reaction for 24 hours, the g-C₃N₄ linker was obtained by centrifugation and used directly in the next step after washing with ethanol. Then, K-SiW₁₁ (6.50 g, 2.02 mmol) was added to the 300 ml aqueous dispersion of the g-C₃N₄ linker. After adjusting the pH to 0.5 with 1 M HCl, the reaction mixture was stirred for 24 hours. The hybrid catalyst of g-C₃N₄–SiW₁₁ was centrifuged, washed with water, and then dried at 60 °C in air. Based on the TGA, EA and ICP analysis, the formula of the catalyst g-C₃N₄ through an organic linker strategy. The organosilicon agent (triethoxysilyl)-propyl isocyanate can act as the linker to covalently combine the SiW₁₁ cluster with g-C₃N₄. The hybrid catalyst g-C₃N₄–SiW₁₁ exhibits efficient catalytic performance (15.2 μmol h⁻¹) for photocatalytic H₂O₂ production in the presence of methanol and can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter). Three reasons have been presented for the efficient catalytic performance of g-C₃N₄–SiW₁₁ from the catalytic and characterization results: 1) the conduction band (CB) level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) is more positive than that of the one-electron reduction of O₂ to 'OH (−0.13 V vs. NHE) and the potential difference between the CB level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) and the O₂ to H₂O₂ potential (0.69 V vs. NHE) is sufficient (0.78 V), which can promote the two-electron reduction of O₂ to H₂O₂; 2) the hybrid catalyst of g-C₃N₄–SiW₁₁ can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter); and 3) most importantly, the experimental and DFT calculation results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can largely enhance the O₂ adsorption of SiW₁₁, which can promote the two-electron reduction of O₂ to H₂O₂.

**Conclusions**

To summarize, to optimize the structure of g-C₃N₄–POMs, the g-C₃N₄ with larger amounts and higher reactivity of –NH₂ groups than 3DOM g-C₃N₄ has been prepared by thermally decomposing urea. The POM cluster of SiW₁₁ with more negative CB level than PW₁₁ has been covalently combined with g-C₃N₄ through an organic linker strategy. The organosilicon agent (triethoxysilyl)-propyl isocyanate can act as the linker to covalently combine the SiW₁₁ cluster with g-C₃N₄. The hybrid catalyst g-C₃N₄–SiW₁₁ exhibits efficient catalytic performance (15.2 μmol h⁻¹) for photocatalytic H₂O₂ production in the presence of methanol and can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter). Three reasons have been presented for the efficient catalytic performance of g-C₃N₄–SiW₁₁ from the catalytic and characterization results: 1) the conduction band (CB) level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) is more positive than that of the one-electron reduction of O₂ to 'OH (−0.13 V vs. NHE) and the potential difference between the CB level of g-C₃N₄–SiW₁₁ (−0.09 V vs. NHE) and the O₂ to H₂O₂ potential (0.69 V vs. NHE) is sufficient (0.78 V), which can promote the two-electron reduction of O₂ to H₂O₂; 2) the hybrid catalyst of g-C₃N₄–SiW₁₁ can stabilize the formed H₂O₂ under sunlight irradiation (AM 1.5 filter); and 3) most importantly, the experimental and DFT calculation results reveal that the covalent combination of SiW₁₁ and g-C₃N₄ can largely enhance the O₂ adsorption of SiW₁₁, which can promote the two-electron reduction of O₂ to H₂O₂.

**Photocatalytic evaluation**

The photocatalytic activities were evaluated by the activation of oxygen under light irradiation. The light source was a 300 W xenon lamp (Perfect Light Company, Beijing), and an AM 1.5 filter was used to simulate sunlight. During each photocatalytic performance, 0.10 g of the catalyst was dispersed into 100 ml of the methanol/water mixture (5/95 v/v) in a container (1 g L⁻¹ catalyst). After that, the dispersion was stirred in the dark for 60 minutes to ensure the adsorption-desorption equilibrium among the catalyst, dissolved oxygen and water before light irradiation. During irradiation, 1.5 ml of the suspension was taken from the reaction cell at given time intervals, and then filtered to remove the catalysts. The liquid-phase products were quantified using a high-performance liquid chromatograph (HPLC; Shimadzu LC-20AT, Tokyo, Japan) equipped with a C18 (250 mm × 4.6 mm × 5 μm) reversed-phase column (GL Sciences Inc., Tokyo, Japan) and a UV detector. The gas-phase product was analyzed using a gas chromatograph (Agilent 7890A) equipped with FID (HP-INNOWAX column) and TCD detectors (Porapack-Q column). The concentrations of the generated H₂O₂ were determined by iodometric titration. After completion of the reaction, the catalysts can be recovered by centrifugation, washed with water, and dried at 60 °C in air. To investigate the decomposition behavior of H₂O₂ over the photocatalysts, a 1 g L⁻¹ sample was dispersed in H₂O₂ solution (initial concentration: 1 mM) and irradiated for 60 minutes under continuous stirring.

**Conflicts of interest**

The authors declare no competing financial interest.

**Acknowledgements**

This work is supported by the National Natural Science Foundations of China (Grant No. 21777176, 21707154, 51578532, and 21647003) and the Chinese Academy of Sciences (QYZDB-SSW-DQC018).

**References**


19 (a) S. Obregón, Y. Zhang and G. Colón, Catalysis Science & Technology, 2016, 6, 3950–3953.


