Covalent combination of polyoxometalate and graphitic carbon nitride for light-driven hydrogen peroxide production

Shen Zhao\textsuperscript{a}, Xu Zhao\textsuperscript{a,*}, Hui Zhang\textsuperscript{b}, Jiang Li\textsuperscript{a}, Yongfa Zhu\textsuperscript{c}

\textsuperscript{a} Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
\textsuperscript{b} State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
\textsuperscript{c} Department of Chemistry, Tsinghua University, Beijing 100084, China

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\section*{ABSTRACT}

The polyoxometalate (POM) cluster of \([\text{PW}_{11}\text{O}_{39}]^{7-}\) (PW\textsubscript{11}) has been successfully covalent combined with the three dimensionally ordered macroporous graphitic carbon nitride (3DOM g-C\textsubscript{3}N\textsubscript{4}) through the organic linker strategy. The characterization such as solid-state NMR and XPS results confirm the organosilicon agent of (triethoxysilyl)-propyl isocyanate can act as the linker to covalent combine the PW\textsubscript{11} cluster with 3DOM g-C\textsubscript{3}N\textsubscript{4}. The hybrid catalyst of 3DOM g-C\textsubscript{3}N\textsubscript{4}-PW\textsubscript{11} exhibits efficient catalytic performance (2.4 \(\mu\)mol h\textsuperscript{-1}) for light-driven \(\text{H}_{2}\text{O}_{2}\) production from \(\text{H}_{2}\text{O}\) and \(\text{O}_{2}\) in the absence of organic electron donors. The ESR results suggest that one-electron reduction of \(\text{O}_{2}\) to \(\cdot\text{OOH}\) is indeed suppressed over 3DOM g-C\textsubscript{3}N\textsubscript{4}-PW\textsubscript{11}. Furthermore, the Koutecky-Levich plot obtained from electrochemical rotating disk electrode (RDE) analysis of oxygen reduction reaction (ORR) for 3DOM g-C\textsubscript{3}N\textsubscript{4}-PW\textsubscript{11} reveals the value of electron transfer during the ORR process is 2.30, indicating the covalent combination can promote the two-electron \(\text{O}_{2}\) reduction. In addition, the recycle experiment results reveal that the heterogeneous 3DOM g-C\textsubscript{3}N\textsubscript{4}-PW\textsubscript{11} is catalytic stable.

\section*{1. Introduction}

Hydrogen peroxide (\(\text{H}_{2}\text{O}_{2}\)) can act as both oxidant and reductant and be widely used in biological process, environmental remediation and chemical industry [1]. As one potential solar fuel, \(\text{H}_{2}\text{O}_{2}\) has several advantages: 1) it is a clean reagent emitting only water as byproduct [2]; 2) it is superior to hydrogen (\(\text{H}_{2}\)) or other fuel gasses due to its convenient and safe storage and transportation in liquid form [3]; and 3) it can be used as a single-compartment direct peroxide-peroxide fuel cell (DPFPC) that is structurally simpler and scales better than the two-compartment \(\text{H}_{2}\) based fuel cells [4]. However, two problems exist in the current \(\text{H}_{2}\text{O}_{2}\) production: 1) the anthraquinone method used in industry catalyzed by Pd-based catalysts requires the regeneration of anthrahydroquinone by \(\text{H}_{2}\) [5a]; and 2) the direct synthesis of \(\text{H}_{2}\text{O}_{2}\) with \(\text{H}_{2}\) and \(\text{O}_{2}\) catalyzed by Pd or Au-Pd catalysts should pay more attention to the potentially explosive nature of \(\text{H}_{2}/\text{O}_{2}\) mixed gases [5b]. A noble metal-free approach capable of producing \(\text{H}_{2}\text{O}_{2}\) without \(\text{H}_{2}\) is therefore desired.

\begin{equation}
\text{H}_{2}\text{O}+2\text{h}^{+}\rightarrow\text{1/2O}_{2}+2\text{H}^{+}(1.23 \text{ V vs. NHE}) 
\end{equation}

\begin{equation}
\text{O}_{2}+2\text{H}^{+}+2\text{e}^{-}\rightarrow\text{H}_{2}\text{O}_{2}(0.68 \text{ V vs. NHE})
\end{equation}

Photocatalytic production of \(\text{H}_{2}\text{O}_{2}\) from \(\text{H}_{2}\text{O}\) and \(\text{O}_{2}\) by semiconductor photocatalysts can meet the above requirement (Eq. (1)) [6]. The solar-to-\(\text{H}_{2}\text{O}_{2}\) conversion can be divided into two half reactions: 1) the photogenerated valence band holes (VB \(\text{h}^{+}\)) oxidizes \(\text{H}_{2}\text{O}\) and produces \(\text{O}_{2}\) and \(\text{H}^{+}\) (Eq. (2)); and 2) two-electron reduction of \(\text{O}_{2}\) by the conduction band electrons (CB \(\text{e}^{-}\)) produces \(\text{H}_{2}\text{O}_{2}\) (Eq. (3)). Among these semiconductor catalysts, graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4})-based catalysts exhibit good efficiency for light-driven \(\text{H}_{2}\text{O}_{2}\) production [6b,e]. However, two problems hinder the improvement of the efficiency for g-C\textsubscript{3}N\textsubscript{4}-based photocatalysts: 1) the fast charge recombination caused intrinsically by the \(\pi-\pi\) conjugated electronic system of g-C\textsubscript{3}N\textsubscript{4} framework [7]; 2) the limited inhibition of the one-electron reduction of \(\text{O}_{2}\) (Eq. (4)) [8]. Therefore, introducing the guest molecules to g-C\textsubscript{3}N\textsubscript{4} host is an effective option to promote the charge separation and the selectivity of the two-electron reduction of \(\text{O}_{2}\) to \(\text{H}_{2}\text{O}_{2}\) [9].
As a class of discrete anionic metal oxides, polyoxometalates (POMs) have been extensively used as photocatalysts for water oxidation [10a], hydrogen evolution [10b], carbon dioxide (CO2) reduction [10c], and selective organic synthesis [10d]. The reason for high performance of the above photocatalytic reactions is that: 1) POMs have strong light absorption with high molecular absorption coefficients ($\varepsilon > 1 \times 10^6 \text{ M}^{-1} \text{ L}^{-1}$) because of the presence of $\pi$$\rightarrow$$\pi^*$ transition; 2) POMs are highly redox-active and can undergo light-induced multi-electron redox-processes due to the high number of metal centres present; and 3) the structural integrity of the cluster shell is maintained during the photoredox processes indicating POMs are catalytic stable [11]. These advantages make POMs the ideal guest molecules for g-C3N4 host. Although POMs have been combined with g-C3N4 [12], these hybrid materials based on the weak interaction such as electrostatic interaction and metal-π conjugation suffer from stability issues owning to POMs leaching [13]. Therefore, the development of covalent combining POMs with g-C3N4 to enhance the interaction between them is highly desirable.

Herein, we have covalent combined the POM cluster of [PW$_{11}$O$_{39}$]$^-$ (PW$_{11}$) with g-C3N4 by taking the organic linker strategy [14]. The primary amine (-NH$_2$) groups of g-C3N4 frameworks can participate in organic reactions to introduce the functional groups to g-C3N4 frameworks [15]. However, the amounts of -NH$_2$ groups on the lamellar g-C3N4 are quite small and the π-π conjugated electronic system of g-C3N4 decreases the reactivity of -NH$_2$ groups, which makes the reaction between the lamellar g-C3N4 and the organic linker difficult under mild conditions [16]. To overcome the above obstacles, three dimensionally ordered macroporous (3DOM) g-C3N4 with interconnected macroporous architecture and large amounts of -NH$_2$ groups have been prepared by the thermal condensation-assisted colloidal crystal template method [17]. Therefore, the organosilicon agent of (triethoxysilyl)-propyl isocyanate can act as the linker to covalent combine the PW$_{11}$ cluster with 3DOM g-C3N4. The hybrid catalyst of 3DOM g-C3N4-PW$_{11}$ with well-defined and stable structure exhibits promoted charge separation and high selectivity of the two-electron reduction of O$_2$ to H$_2$O$_2$. After adjusting the pH to 0.5 with 1 M HCl, the reaction mixture was stirred for 24 h. The hybrid catalyst of 3DOM g-C3N$_4$-PW$_{11}$ was centrifuged, washed by water, and then dried at 60 °C in air. Based on the TGA, EA and ICP analysis, the formula of 3DOM g-C3N$_4$-PW$_{11}$ was determined to be C$_{24.44}$N$_{4.53}$H$_{1.57}$ (K$_3$PW$_{11}$O$_{42}$Si$_2$C$_8$H$_{14}$N$_2$)$_{0.021}$ (40.41 wt% PW$_{11}$). For comparison, 3DOM g-C$_3$N$_4$-PW$_{11}$-IMP based on the electrostatic interaction has been prepared through the impregnation method with the same PW$_{11}$ weight percentage as 3DOM g-C$_3$N$_4$-PW$_{11}$ based on covalent interaction.

### 2.4. Photocatalytic evaluation

The photocatalytic activities were evaluated by the activation of oxygen under light irradiation (λ > 320 nm) [6a]. A 300 W Xenon lamp (Perfect Light company, Beijing) was chosen as light source. During each photocatalytic performance, 0.10g of catalyst was dispersed into 100 ml of distilled water in a container (1g L$^{-1}$ catalyst). After that, the dispersion was stirred in the dark for 60 min to ensure the adsorption-desorption equilibrium among the catalyst, dissolved oxygen and water before light irradiation. During the irradiation, 1.5 ml of the suspensions was taken from the reaction cell at given time intervals, and then filtrated to remove the catalysts. The concentrations of H$_2$O$_2$ generated were determined by iodometric titration [21]. 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 H$_2$O$_2$ over the photocatalysts, a sample of 1g L$^{-1}$ was dispersed in H$_2$O$_2$ solution (initial concentration: 1 mM) and irradiated for 60 min under continuous stirring.

### 2.5. Rotating disk electrode (RDE) measurements

The measurements were performed on a Pine AFM/SRXE 1523 advanced electrochemical system with a three-electrode cell using an Ag/AgCl electrode and a Pt wire electrode as the reference and counter electrode, respectively [6e]. The working electrode was prepared as follows: catalysts (50 mg) were dispersed in EIOH (2 ml) containing Nafion (50 mg) by ultrasonication. The slurry (20 µl) was put onto a Pt disk electrode and dried at room temperature. The linear sweep voltammogram (LSV) were obtained in an O$_2$-saturated 0.1 M phosphate buffer solution (pH 7) with a scan rate 10 mV s$^{-1}$ after O$_2$ bubbling for 5 min.

### 2.6. OOH radical examination

• OOH was examined by a Bruker model electron spin resonance (ESR) A300-10/12 spectrometer equipped with a quanta-Ray Nd: YAG laser system employing 5.5-dimethyl-l-pyrroline-N-oxide (DMPO) as the spin trapper. Catalyst (0.10 g) was added to a methanol/water mixture (9/1 v/v, 100 ml) containing DMPO (0.125 mmol) within a container. After O$_2$ bubbling for 10 min, the container was photo irradiated for 3 min. The catalyst was recovered by filtration, and the solution was subjected to analysis at room temperature.
3. Results and discussion

3.1. Covalent combination of PW11 and 3DOM g-C3N4

The covalent combination of POM cluster of PW11 and 3DOM g-C3N4 has been achieved by taking the organic linker strategy [14]. The 3DOM g-C3N4 with interconnected macroporous architecture and larger amounts of -NH2 groups than those of lamellar g-C3N4 (Fig. S1) have been prepared by the thermal condensation-assisted colloidal crystal template method [17]. As shown in Fig. 1, the organosilicon linkers can be grafted onto 3DOM g-C3N4 through the formation of carbamido groups to generate the 3DOM g-C3N4 linker. The POM cluster of PW11 can covalent connect with 3DOM g-C3N4 linker under acidic solution following the reported method [19]. In this way, the POM cluster of PW11 has been covalent combined with 3DOM g-C3N4 to form the hybrid catalyst of 3DOM g-C3N4-PW11 for light-driven H2O2 production from H2O and O2.

3.2. Characterization of 3DOM g-C3N4-PW11

The covalent combination of PW11 and 3DOM g-C3N4 has been firstly confirmed by solid-state NMR. The 13C MAS NMR spectrum of 3DOM g-C3N4 (Fig. 2A) exhibits two typical signal groups of the g-C3N4: the first signal groups at 163.0 and 165.1 ppm with a 1.9:1 intensity ratio are the resonances for the CN2(NH2) groups, and the second signal groups at 156.8 ppm belong to the CN3 groups of the cyameluric nucleus [22]. In contrast, the 13C MAS NMR spectrum of 3DOM g-C3N4-PW11 (Fig. 2A) shows not only the two typical signal groups of 3DOM g-C3N4 but also the signal groups at 9.8 ppm assigned to the organosilicon linker. The presence of the signal at 9.8 ppm confirms the organosilicon linker has been covalent linked with 3DOM g-C3N4. The 29Si MAS NMR spectrum of 3DOM g-C3N4-PW11 (Fig. 2B) displays resonance peaks centered at ~64.9 ppm, which corresponds to RSi(OM)3 (T3 mode, R=CH2CH2CH2NH(CO)-, M=Si or W) [19a]. The presence of the T3 signal reveals that three M-O-Si (M=Si or W) bonds around the Si atom, which confirms that the organosilicon linker are covalently tethered onto the vacancy of PW11 cluster [19b]. The above 13C and 29Si MAS NMR results confirm that the PW11 cluster has been successfully covalent combined with 3DOM g-C3N4 by the organosilicon linker. The similar signals at around ~13.7 and ~13.4 ppm of the 31P MAS NMR for K-PW11 and 3DOM g-C3N4-PW11 (Fig. 2C) reveal that the primary structure of PW11 cluster has been well preserved after covalent combination [13]. More characterization should be performed to investigate the structure and composition of 3DOM g-C3N4-PW11.

The XRD pattern of 3DOM g-C3N4, K-PW11 and 3DOM g-C3N4-PW11 is shown in Fig. S2. The diffraction peaks located at 12.9° and 27.4° of 3DOM g-C3N4 are assigned to the g-C3N4 with (100) and (002) lines, which come from in-plane repeating tri-s-triazine and stacking of the conjugated aromatic units, respectively [23]. For 3DOM g-C3N4-PW11, the weak intensity of characteristic peaks at 27.4° and the presence of typical PW11-related peaks in the range of 8–11° indicates that the PW11 cluster has been successfully covalent combined with 3DOM g-C3N4 through the organosilicon linker [12a,b,d]. Fig. S3 shows the IR spectrum of 3DOM g-C3N4, K-PW11 and 3DOM g-C3N4-PW11. The peaks in the range of 1180–1755 cm⁻¹ have been observed in both 3DOM g-C3N4 and 3DOM g-C3N4-PW11, which are the typical vibrations of hepatizine-based molecular units [12c]. The vibrations at 1067, 983, and 892 cm⁻¹ corresponding to chemical bonds of W=C=O, P-O, and W-O-W in the Keggin POM of PW11 can be found in both K-PW11 and 3DOM g-C3N4-PW11 [24]. The above IR results indicates that the primary structure of 3DOM g-C3N4 and PW11 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 [15], indicating the decreased content of surface 
-NH2 groups in 3DOM g-C3N4-PW11. CO2 temperature programmed 
desorption (CO2-TPD) has been performed to investigate the temperature 
range of 150 °C, and the loss of physisorbed water and crystallization water and the weight 
loss in the range of 50 °C is much smaller than that of 3DOM g-C3N4. Furthermore, the zeta 
potentials of aqueous suspension of 3DOM g-C3N4 and 3DOM g-C3N4-PW11 has been measured because the -NH2 groups with the free 
loner pair electrons on nitrogen atoms can act as proton acceptors and acquire positive surface charges [26]. Fig. S5 shows the zeta potential of 3DOM g-C3N4 and 3DOM g-C3N4-PW11 after covalent combination, confirming the reaction between the -NH2 groups of 3DOM g-C3N4 and the organosilicon linkers. The isotherms of 3DOM g-C3N4 and 3DOM g-C3N4-PW11 (Fig. S6A) are consistent with type II isotherm with a type H3 hysteresis loop in the relative 
pressure (P/P0) range of 0.6–1.0 according to IUPAC classification. These two catalysts present a broad pore-size distribution curve (2–132 nm) from mesopore range to macropore range (Fig. S6B). The above results confirm both 3DOM g-C3N4 and 3DOM g-C3N4-PW11 possesses clear macroporous structure [27]. The surface area, pore volume and pore diameter of 3DOM g-C3N4 and 3DOM g-C3N4-PW11 are shown in Table S1. Compared with 3DOM g-C3N4, the decrease in these values of 3DOM g-C3N4-PW11 is due to the covalent combination of PW11 cluster and the macroporous structure of 3DOM g-C3N4 [12a,d,d]. Thermogravimetry analysis (TGA) curves for 3DOM g-C3N4, K-PW11 and 3DOM g-C3N4-PW11 are shown in Fig. S7. The total weight loss of 3DOM g-C3N4 is 93.67% between 50 and 800 °C due to the direct thermal decomposition of 3DOM g-C3N4. For K-PW11, the weight loss in the range of 50–150 °C range (2.14%) corresponds to the loss of physisorbed water and crystallization water and the weight loss in the range of 150–600 °C (2.78%) is assigned to the Keggin structure decomposition [24]. According to the above results, the actual weight percentage of PW11 cluster for 3DOM g-C3N4 is 40.41%. Combining the TGA, EA and ICP analysis (Table S2), the molecular formulas of 3DOM g-C3N4, and 3DOM g-C3N4-PW11 can be given as C2.44N4H1.57 and C2.44N4H1.53(K3PW11O42Si2C8H14N2)0.021. As shown in Fig. 3A, XPS peaks of C 1 s for 3DOM g-C3N4 and 3DOM g-C3N4-PW11 can be fitted with two peaks at binding energies of around 284.2 and 287.6 eV, which are ascribed to the C-C groups and the tertiary carbon C-N3, respectively [8b]. The area ratios of these two peaks are 0.26 and 2.41 for 3DOM g-C3N4 and 3DOM g-C3N4-PW11. The tremendous increase of the C-C groups supports the organosilicon linker has been covalent linked with 3DOM g-C3N4. Nevertheless, the XPS peaks of N 1 s (Fig. 3B) for 3DOM g-C3N4 can be fitted with three peaks at 398.0, 399.6, and 404.2 eV, which are assigned to the N-(C2), N-(C3) and -NH2, respectively [8b]. However, the 3DOM g-C3N4-PW11 only exhibits two peaks at 398.4 and 399.7 eV corresponding to N-(C2) and N-(C3). The disappearance of -NH2 peak indicates that the -NH2 groups of 3DOM g-C3N4 react with NCO- groups of silane coupling agent to form the carbamido groups during the covalent combination of PW11 cluster with 3DOM g-C3N4. The above results confirm the PW11 cluster has been well preserved after covalent combination. XPS peaks of O 1 s (Fig. 3C) for 3DOM g-C3N4-PW11 shows one peak at 101.8 eV corresponding to R-Si-(O 3)( R = CH3CH2CH2NH(CO2)-), which is in accordance with 29Si MAS NMR result of 3DOM g-C3N4-PW11 [28]. Both the 3DOM g-C3N4 and K-PW11 and 3DOM g-C3N4-PW11 show one P 2p XPS peak at 133.3 eV (Fig. 3D). In addition, XPS peaks of W 4 f (Fig. 3E) for 3DOM g-C3N4-PW11 can be fitted with two peaks at binding energies of around 34.9 and 37.1 eV (W 4 f7/2 and W 4f5/2), which are consistent with a W(VI) oxidation state [13]. The P 2p and W 4 f XPS results reveal that the primary structure of PW11 cluster has been well preserved after covalent combination. XPS peaks of O 1 s (Fig. 3F) for K-PW11 and 3DOM g-C3N4-PW11 can be fitted with two peaks at binding energies of around 531.3 and 530.0 eV, which are ascribed to the W-O-O-W/Si and WO, respectively [12c]. The area ratios of these two peaks are 0.51 and 1.06 for K-PW11 and 3DOM g-C3N4-PW11. The largely increase of the W-O-O-W/Si supports the organosilicon linker are covalently tethered onto the vacancy of PW11 cluster. The above XPS results confirm the PW11 cluster has been covalent combination with 3DOM g-C3N4 through the organosilicon linker and the primary structure of PW11 cluster has been well preserved after covalent combination.

Fig. S8 are the TEM images of 3DOM g-C3N4 (Fig. S8A–C) and
3DOM g-C₃N₄-PW₁₁ (Fig. S8D–F), which exhibit interconnected macroporous architecture with the average pore diameter of 260–350 nm [17]. However, PW₁₁ clusters cannot be observed obviously in the HR-TEM images of 3DOM g-C₃N₄-PW₁₁ (Fig. S8D–F), mainly due to the PW₁₁ clusters are highly dispersed on 3DOM g-C₃N₄ [12a,b,d]. To investigate the dispersion of PW₁₁ on 3DOM g-C₃N₄, STEM-Mapping characterization has been performed. As shown in Fig. 4A, 3DOM g-C₃N₄-PW₁₁ remains the macroporous structure after covalent combination. The STEM image in Fig. 4B shows a rough defect-rich surface with curvatures, distortions, protuberances, and crumpled edges [12c]. The elemental mappings of C, N, O, and W (Fig. 4C–G) clearly exhibit the PW₁₁ clusters are highly dispersed on the surface of 3DOM g-C₃N₄ after covalent combination.

The above characterization results confirm that the PW₁₁ cluster has been covalent combined with 3DOM g-C₃N₄ to form the hybrid catalyst of 3DOM g-C₃N₄-PW₁₁. Furthermore, the catalytic performance of 3DOM g-C₃N₄-PW₁₁ should be investigated.

### 3.3. Catalytic performance of 3DOM g-C₃N₄-PW₁₁

The light-driven H₂O₂ production over various catalysts has been conducted and monitored in an O₂-equilibrated conditions and light irradiation (λ≥320 nm) in the absence of organic electron donors at 25 °C. As shown in Fig. 5A, the H₂O₂ can be rapidly generated over 3DOM g-C₃N₄-PW₁₁, and the amounts of formed H₂O₂ can reach 3.5 μmol in 60 min. The catalytic performance of only 3DOM g-C₃N₄ (1.3 μmol in 60 min) or K-PW₁₁ ( < 0.1 μmol in 60 min) is lower than that of 3DOM g-C₃N₄-PW₁₁ (3.5 μmol in 60 min). For comparison, 3DOM g-C₃N₄-PW₁₁-IMP based on the electrostatic interaction has been prepared through the impregnation method with the same PW₁₁ weight percentage as 3DOM g-C₃N₄-PW₁₁ based on covalent interaction. 3DOM g-C₃N₄-PW₁₁-IMP shows lower catalytic performance (1.5 μmol in 60 min). The reaction cannot proceed in the absence of catalyst ( < 0.1 μmol in 60 min). When extending the reaction time to 360 min, the maximum amounts of formed H₂O₂ over 3DOM g-C₃N₄-PW₁₁, 3DOM g-C₃N₄-PW₁₁-IMP and 3DOM g-C₃N₄ can be obtained as 14.4, 5.2 and 2.3 μmol, respectively (Fig. S9), which gives the H₂O₂ formation rate of 2.4, 0.9 and 0.4 μmol h⁻¹ for 3DOM g-C₃N₄-PW₁₁, 3DOM g-C₃N₄-PW₁₁-IMP and 3DOM g-C₃N₄.

(Table S3). Fig. S10 shows the lamellar g-C₃N₄ shows no catalytic performance ( < 0.1 μmol in 60 min) because 3DOM g-C₃N₄ with macroporous structure has large amounts of -NH₂ groups that are active for light-driven H₂O₂ production (Fig. S1) [8b,29].

The formation and decomposition of H₂O₂ over catalysts proceeds through two competitive pathways owing to the thermodynamic instability of H₂O₂ at room temperature [6a,30]. We therefore separately evaluate the rate constants for light-driven H₂O₂ formation and decomposition by assuming zero-order and first-order kinetics [31]:

\[
[H₂O₂] = \frac{K_f}{K_d} (1 - e^{-K_d t})
\]

The Kₚ and Kᵩ values have been estimated by fitting the data in...
Fig. 6. Light-driven H2O2 decomposition over different catalysts. Reaction conditions: H2O2 solution (100 ml, initial concentration=1 mM), catalyst (0.10 g, 1 g L−1), λ=320 nm, 25 °C.

Table 1

| Catalyst          | Maximum formed H2O2 (μmol) | H2O2 Formation Rate (μmol h−1) | Refs. |
|-------------------|-----------------------------|-------------------------------|-------|
| 3DOM g-C3N4       | 14.4                        | 2.4                           | This work |
| g-C3N4-BDI50      | 11.6                        | 0.5                           | [35]   |
| g-C3N4-PDI51      | 50.6                        | 1.0                           | [6b]   |
| rGOs              | 30.0                        | 1.2                           | [6e]   |
| g-C3N4-NiFeO      | 1.8                         | 1.8                           | [32]   |
| Cv-g-C3N4         | 9.2                         | 9.2                           | [86]   |

*BDI=biphenyl diimide; 
*PDI=promellitic diimide; 
*rGOs=reduced graphene oxide; 
*Cv-g-C3N4=carbon vacancy contained g-C3N4.*

3.4. Structure-catalytic performance relationship of 3DOM g-C3N4-PW11

Photocatalytic characterization should be performed to clarify the reason for the efficient activity of 3DOM g-C3N4-PW11. The catalysts of 3DOM g-C3N4 and 3DOM g-C3N4-PW11 have been casted on fluorine-doped tin oxide (FTO) electrodes and these electrodes have been used in a three-electrode electrochemical cell [32]. As shown in Fig. S1A, the photo-current density of 3DOM g-C3N4-PW11 (0.43 μA cm−2) is much larger than that of 3DOM g-C3N4 (0.01 μA cm−2). Photocatalytic impedance spectroscopy (EIS) results are shown in Fig. S1B. The diameter of Nyquist semicircle for 3DOM g-C3N4-PW11 is smaller than that of 3DOM g-C3N4, which indicates that the 3DOM g-C3N4-PW11 composites have lower resistances than 3DOM g-C3N4. The above results reveal that the covalent combination of PW11 and 3DOM g-C3N4 can enhance the charge separation of 3DOM g-C3N4-PW11. Photoluminescence (PL) spectrum has been used to explore the recombination and separation of photo-generated electrons and holes in the 3DOM g-C3N4 and 3DOM g-C3N4-PW11 (Fig. S1A). The emission peak appearing at about 485 nm is attributed to the direct electron-hole recombination of band transition. Compare with 3DOM g-C3N4, 3DOM g-C3N4-PW11 possess a weaker emission peak, confirming the above photo-current and EIS results.

The above catalytic and characterization results indicate that the covalent combination of PW11 cluster and 3DOM g-C3N4 can enhance the charge separation and thus facilitate the light-driven formation of H2O2. Furthermore, the above results also suggest that the 3DOM g-C3N4-PW11 can act as a dual-functional catalyst for both water oxidation and oxygen reduction reactions [32]. Nevertheless, the H2O2 formation rate (2.4 μmol h−1) over 3DOM g-C3N4-PW11 is more than those over TiO2-CoPi-rGOs [6a] and (0.5 μmol h−1) over Cds-rGOs [6b]. Therefore, the relative high H2O2 formation rate among the reported catalysts make 3DOM g-C3N4-PW11 a promising catalyst for light-driven H2O2 production in the absence of organic electron donors.

It is important to note that under similar reaction conditions over the g-C3N4-based catalysts in the absence of organic electron donors (Table 1), the H2O2 formation rate (2.4 μmol h−1) over 3DOM g-C3N4-PW11 is more than those over (0.5 μmol h−1) g-C3N4-BDI50 [35], (1.0 μmol h−1) g-C3N4-PDI51 [6b], (1.2 μmol h−1) g-C3N4-PDI11-rGOs [6e], and (1.8 μmol h−1) g-C3N4-NiFeO [32], but inferior to that (9.2 μmol h−1) over Cv-g-C3N4 [86]. Though Cv-g-C3N4 shows better catalytic performance for two-electron O2 reduction to H2O2 than 3DOM g-C3N4-PW11, the ability of water oxidation for Cv-g-C3N4 is negligible where H2O2 cannot be detected under Ar-equilibrated conditions [86]. On the contrary, 3DOM g-C3N4-PW11 can produce considerable amounts of H2O2 (1.5 μmol in 60 min) under N2-equilibrated conditions (Fig. S12), indicating the 3DOM g-C3N4-PW11 can act as a dual-functional catalyst for both water oxidation and oxygen reduction [32]. Nevertheless, the H2O2 formation rate (2.4 μmol h−1)
oxidation and oxygen reduction. Therefore, the catalytic performance for water oxidation and oxygen reduction should be investigated. The water oxidation performance has been evaluated by oxygen evolution reaction (OER) \([6a,32]\). Fig. 7A shows linear sweep voltammogram (LSV) curves of the electrodes with the 3DOM g-C\(_3\)N\(_4\) and 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) in the dark. The onset potential of 3DOM g-C\(_3\)N\(_4\) is at approximately 1.93 V vs. normal hydrogen electrode (NHE) in the dark, which had a 0.70 V overpotential because the thermodynamic potential was 1.23 V vs. NHE. In addition, the slow increase of the current density at -0.9 V vs. Ag/AgCl. The average number of electrons \((n)\) involved in the overall O\(_2\) reduction can be estimated by the linear regression of the plots using the following equations \([37]\):

\[
j = j_0^{-1} + B^{-1}\omega^{-1/2}
\]

\[
B = 0.2nFv^{-1/6}CD^{2/3}
\]

\(j\) is the current density, \(j_0\) is the kinetic current density, \(\omega\) is the rotating speed (rpm), \(F\) is the Faraday constant (96485 C mol\(^{-1}\)), \(v\) is the kinetic viscosity of water (0.01 cm\(^2\) s\(^{-1}\)), \(C\) is the bulk concentration of O\(_2\) in water (2.7×10\(^{-3}\) mol cm\(^{-3}\)), and \(D\) is the diffusion coefficient of O\(_2\) (2.7×10\(^{-5}\) cm\(^2\) s\(^{-1}\)), respectively \([37]\). The n value for 3DOM g-C\(_3\)N\(_4\) (n=1.85) suggests that one-electron O\(_2\) reduction indeed occurs, which confirms the ESR results. In contrast, 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) exhibits n=2.30, indicating the covalent combination of 3DOM g-C\(_3\)N\(_4\) and PW\(_{11}\) can selectively promote the two-electron O\(_2\) reduction.

The flat band potentials (\(E_{fb}\)) of 3DOM g-C\(_3\)N\(_4\) and 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) casted on FTO has been estimated by electrochemical Mott-Schottky measurements at varied frequencies (1.0, 1.5 and 2.0 kHz). The Mott-Schottky plots of both catalysts exhibit positive slopes (Fig. S15) at band potentials (\(E_{fb}\)) of 3DOM g-C\(_3\)N\(_4\) and 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\), indicating the amounts of Oads in 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) are much more than those in 3DOM g-C\(_3\)N\(_4\) and K-PW\(_{11}\). Combining the ESR, Koutecky-Levich plots and O\(_2\)-TPD results, the enhanced O\(_2\) adsorption of catalysts can promote the multi-electron reduction of O\(_2\) \([36,38]\). Furthermore, O\(_2\) temperature programmed desorption (O\(_2\)-TPD) has been performed to detect the changes of oxygen species after the covalent combination (Fig. S16). The oxygen desorption at low temperature (< 400 °C) is ascribed to adsorbed oxygen (O\(_{ads}\)), and the lattice oxygen (O\(_{latt}\)) starts to be released at high temperature (> 400 °C) \([27]\). The oxygen desorption at 341 °C can only be observed in 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\), indicating the amounts of O\(_{ads}\) in 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) are much more than those in 3DOM g-C\(_3\)N\(_4\) and K-PW\(_{11}\). Combining the ESR, Koutecky-Levich plots and O\(_2\)-TPD results, the enhanced O\(_2\) adsorption of 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) can selectively promote the two-electron reduction of O\(_2\) to H\(_2\)O\(_2\).

The flat band potentials (\(E_{fb}\)) of 3DOM g-C\(_3\)N\(_4\) and 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\) casted on FTO has been estimated by electrochemical Mott-Schottky measurements at varied frequencies (1.0, 1.5 and 2.0 kHz). The Mott-Schottky plots of both catalysts exhibit positive slopes (Fig. S17A and B), suggestive of their n-type semiconductor features \([39]\). The \(E_{fb}\) values have been estimated by extrapolating the linear portion of the curve to intercept of the X-axis \([40]\). The flat band potential of -0.15 V and 0.06 V vs. NHE has been obtained for 3DOM g-C\(_3\)N\(_4\) and 3DOM g-C\(_3\)N\(_4\)-PW\(_{11}\), respectively. The conduction band could be 0–0.1 V more negative than the flat band position. Hence, the corre-
sponding CB edge of 3DOM g-C$_3$N$_4$ and 3DOM g-C$_3$N$_4$-PW$_{11}$ has been estimated to be $-0.25$ V and $-0.04$ V vs. NHE, respectively. A positive shift of 0.21 V from 3DOM g-C$_3$N$_4$ to 3DOM g-C$_3$N$_4$-PW$_{11}$ has been observed. The positive shift of the CB in 3DOM g-C$_3$N$_4$-PW$_{11}$ is likely to improve the selectivity of O$_2$ reduction to H$_2$O$_2$ [6c]. The Tauc plots of 3DOM g-C$_3$N$_4$ and 3DOM g-C$_3$N$_4$-PW$_{11}$ have been derived according to the relationship of $(F(R)·V)^2=A(hv-E_g)$, where $h$ is Planck’s constant, $v$ is the frequency, $A$ is a constant, and $E_g$ is the material band gap (Fig. S14C) [41]. From the Tauc plots, the band gap of 3DOM g-C$_3$N$_4$ and 3DOM g-C$_3$N$_4$-PW$_{11}$ are 2.82 and 2.78 eV, respectively.

Combining the Mott-Schottky measurements and Tauc plots results, the VB positions of 3DOM g-C$_3$N$_4$ and 3DOM g-C$_3$N$_4$-PW$_{11}$ have been estimated as 2.57 V and 2.74 V vs. NHE, respectively. As shown in Fig. 7D, both the CB and VB of 3DOM g-C$_3$N$_4$-PW$_{11}$ are more positive than those of 3DOM g-C$_3$N$_4$. Because the water oxidation is a rate-limiting step, the positive shift of the VB in the 3DOM g-C$_3$N$_4$-PW$_{11}$ facilitates to overcome the kinetic barrier of the O$_2$ evolution. Moreover, the CB level in 3DOM g-C$_3$N$_4$-PW$_{11}$ (-0.04 V vs. NHE) is more positive than the one-electron reduction of O$_2$ to *OOH (-0.13 V vs. NHE), and has sufficient potential difference (0.73 V) from the two-electron reduction of O$_2$ to H$_2$O$_2$ (0.69 V vs. NHE) [42]. The results are in accordance with the reported g-C$_3$N$_4$-PDI and g-C$_3$N$_4$-NiFeO$_2$ catalysts, in which both the CB and VB levels of g-C$_3$N$_4$-PDI and g-C$_3$N$_4$-NiFeO$_2$ are shifted positively [6c,32]. In these catalytic systems, the positive shifts of VB have proved to enhance the capability of 3DOM g-C$_3$N$_4$-PW$_{11}$ for water oxidation and promote the two-electron reduction of O$_2$ to H$_2$O$_2$.

### 3.5. Recycle of heterogeneous 3DOM g-C$_3$N$_4$-PW$_{11}$

It is essential to confirm the catalysis of 3DOM g-C$_3$N$_4$-PW$_{11}$ is truly heterogeneous for light-driven H$_2$O$_2$ production. When the reaction time arrives at 30 min, 3DOM g-C$_3$N$_4$-PW$_{11}$ has been removed from the reaction system by filtration, and the reaction is allowed to proceed with the filtrate under the same conditions as shown in Fig. 8A, no new H$_2$O$_2$ forms and the formed H$_2$O$_2$ starts to decompose under the same conditions. Furthermore, the ICP-AES result reveals no W leaching in the filtrate. The above results rule out the contribution of W species leached into the reaction solution for the observed catalytic results and confirm the 3DOM g-C$_3$N$_4$-PW$_{11}$ is truly heterogeneous for H$_2$O$_2$ production.

To investigate the stability of heterogeneous 3DOM g-C$_3$N$_4$-PW$_{11}$, the light-driven production of H$_2$O$_2$ has been recycled for five times under the same conditions. Fig. 8B shows the catalytic performance is almost unchanged and the catalyst recovery can reach above 96% even after five times. The XRD, IR, $^{13}$C, $^{29}$Si and $^{31}$P MAS NMR spectra of the fresh and used 3DOM g-C$_3$N$_4$-PW$_{11}$ exhibits almost the same typical peaks (Figs. S11, S18 and S19). The STEM-Mapping results of the used 3DOM g-C$_3$N$_4$-PW$_{11}$ (Fig. S20) indicates that the macroporous structure and the dispersion of PW$_{11}$ cluster on 3DOM g-C$_3$N$_4$ are retained after reaction. The EA and ICP results in Table S2 also reveal that the composition of the used 3DOM g-C$_3$N$_4$-PW$_{11}$ remains unchanged. The above results indicate that the heterogeneous 3DOM g-C$_3$N$_4$-PW$_{11}$ is catalytic stable.

### 4. Conclusions

To summarize, the hybrid catalyst of 3DOM g-C$_3$N$_4$-PW$_{11}$ with well-defined and stable structure has been prepared by covalent combining the PW$_{11}$ cluster with 3DOM g-C$_3$N$_4$ through the organic linker strategy. The organosilicon agent of (triethoxysilyl)-propyl isocyanate can act as the linker to covalent combine the PW$_{11}$ cluster with 3DOM g-C$_3$N$_4$. The hybrid catalyst of 3DOM g-C$_3$N$_4$-PW$_{11}$ exhibits efficient catalytic performance for light-driven H$_2$O$_2$ production from H$_2$O and O$_2$ in the absence of organic electron donors. The catalytic and characterization results suggest the three reasons for the efficient catalytic performance of 3DOM g-C$_3$N$_4$-PW$_{11}$: 1) the covalent combination of PW$_{11}$ cluster and 3DOM g-C$_3$N$_4$ can enhance the charge separation of photogenerated holes and electrons; 2) the more positive potential of the valence band (VB) under the covalent combination can elevate photogenerated holes separation and involvement in water oxidation; 3) the conduction band (CB) level of 3DOM g-C$_3$N$_4$-PW$_{11}$ (-0.04 V vs. NHE) is more positive than that of the one-electron reduction of O$_2$ to *OOH (-0.13 V vs. NHE), and the potential difference between the CB level of 3DOM g-C$_3$N$_4$-PW$_{11}$ (-0.04 V vs. NHE) and O$_2$ to H$_2$O$_2$ potential (0.69 V vs. NHE) is sufficient (0.73 V), which can promote the two-electron reduction of O$_2$ to H$_2$O$_2$. In addition, the recycle experiment results reveal that the heterogeneous 3DOM g-C$_3$N$_4$-PW$_{11}$ is catalytic stable. The covalent combination of POMs and g-C$_3$N$_4$ opens the door for further exploration and design of multifunctional catalytic materials tailored for specific applications.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.04.017.

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Shen Zhao obtained his Ph.D. degree in science of drinking water science and technology at Beijing University of Chemical and Technology in 2014. Now he is an Assistant Professor in Key Laboratory of Drinking Water Science and Technology at Research Center for Eco-Environmental Sciences of Chinese Academy of Sciences. His research interests focus on materials chemistry and photocatalysis.

Xu Zhao obtained his Ph.D. degree in Department of environmental science and technology at Dalain University of Technology in 2004. Now he is a Professor in Key Laboratory of Drinking Water Science and Technology at Research Center for Eco-Environmental Sciences of Chinese Academy of Sciences and University of Chinese Academy of Sciences. His research interest involves electrochemistry, photocatalysis and water treatment.
**Hui Zhang** obtained his Ph.D. degree in Department of environmental science and technology at Dalian University of Technology in 2011. Now he is an Associate Professor in State Key Laboratory of Environmental Chemistry and Ecotoxicology at Research Center for Eco-Environmental Sciences of Chinese Academy of Sciences. His research interests focus on materials chemistry and photocatalysis.

**Jiang Li** is a joint training Master candidate in School of Light Industry and Chemical Engineering at Dalian Polytechnic University and Key Laboratory of Drinking Water Science and Technology at Research Center for Eco-Environmental Sciences of Chinese Academy of Sciences. His research interests focus on photocatalysis.

**Yongfa Zhu** obtained his Ph.D. degree in Chemistry Department at Tsinghua University in 1995. Now he is a Professor in Chemistry Department at Tsinghua University. His research interests focus on surface chemistry, materials chemistry and photocatalysis.