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

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ABSTRACT

The polyoxometalate (POM) cluster of $[PW_{11}O_{39}]^{7-}$ (PW_{11}) has been successfully covalently combined with the three dimensionally ordered macroporous graphitic carbon nitride (3DOM g-C₃N₄) 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 covalently combine the PW_{11} cluster with 3DOM g-C₃N₄. The hybrid catalyst of 3DOM g-C₃N₄- PW_{11} exhibits efficient catalytic performance ($2.4 \mu\text{mol h}^{-1}$) for light-driven H₂O₂ production from H₂O and O₂ in the absence of organic electron donors. The ESR results suggest that one-electron reduction of O₂ to $\cdot\text{OOH}$ is indeed suppressed over 3DOM g-C₃N₄- PW_{11} . Furthermore, the Koutecky-Levich plot obtained from electrochemical rotating disk electrode (RDE) analysis of oxygen reduction reaction (ORR) for 3DOM g-C₃N₄- PW_{11} reveals the value of electron transfer during the ORR process is 2.30, indicating the covalent combination can promote the two-electron O₂ reduction. In addition, the recycle experiment results reveal that the heterogeneous 3DOM g-C₃N₄- PW_{11} is catalytically stable.

1. Introduction

Hydrogen peroxide (H₂O₂) 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, H₂O₂ has several advantages: 1) it is a clean reagent emitting only water as byproduct [2]; 2) it is superior to hydrogen (H₂) or other fuel gases 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 (DPPFC) that is structurally simpler and scales better than the two-compartment H₂ based fuel cells [4]. However, two problems exist in the current H₂O₂ production: 1) the anthraquinone method used in industry catalyzed by Pd-based catalysts requires the regeneration of anthrahydroquinone by H₂ [5a]; and 2) the direct synthesis of H₂O₂ with H₂ and O₂ catalyzed by Pd or Au-Pd catalysts should pay more attention to the potentially explosive nature of H₂/O₂ mixed gases [5b]. A noble metal-free approach capable of producing H₂O₂ without H₂ is therefore desired.

Photocatalytic production of H₂O₂ from H₂O and O₂ by semiconductor photocatalysts can meet the above requirement (Eq. (1)) [6]. The solar-to-H₂O₂ conversion can be divided into two half reactions: 1) the photogenerated valence band holes (VB h⁺) oxidizes H₂O and produces O₂ and H⁺ (Eq. (2)); and 2) two-electron reduction of O₂ by the conduction band electrons (CB e⁻) produces H₂O₂ (Eq. (3)). Among these semiconductor catalysts, graphitic carbon nitride (g-C₃N₄)-based catalysts exhibit good efficiency for light-driven H₂O₂ production [6b,e]. However, two problems hinder the improvement of the efficiency for g-C₃N₄-based photocatalysts: 1) the fast charge recombination caused intrinsically by the π - π conjugated electronic system of g-C₃N₄ framework [7]; 2) the limited inhibition of the one-electron reduction of O₂ (Eq. (4)) [8]. Therefore, introducing the guest molecules to g-C₃N₄ host is an effective option to promote the charge separation and the selectivity of the two-electron reduction of O₂ to H₂O₂ [9].

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As a class of discrete anionic metal oxides, polyoxometalates (POMs) have been extensively used as photocatalysts for water oxidation [10a], hydrogen evolution [10b], carbon dioxides (CO_2) 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 ($\epsilon > 1 \times 10^4\text{ M}^{-1}\text{ L}^{-1}$) because of the presence of O→M ligand-to-metal charge transfer (LMCT) bands; 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 $\text{g-C}_3\text{N}_4$ host. Although POMs have been combined with $\text{g-C}_3\text{N}_4$ [12], these hybrid materials based on the weak interaction such as electrostatic interaction and metal-ligand coordination suffer from stability issues owing to POMs leaching [13]. Therefore, the development of covalent combining POMs with $\text{g-C}_3\text{N}_4$ to enhance the interaction between them is highly desirable.

Herein, we have covalent combined the POM cluster of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (PW_{11}) with $\text{g-C}_3\text{N}_4$ by taking the organic linker strategy [14]. The primary amine ($-\text{NH}_2$) groups of $\text{g-C}_3\text{N}_4$ frameworks can participate in organic reactions to introduce the functional groups to $\text{g-C}_3\text{N}_4$ frameworks [15]. However, the amounts of $-\text{NH}_2$ groups on the lamellar $\text{g-C}_3\text{N}_4$ are quite small and the π - π conjugated electronic system of $\text{g-C}_3\text{N}_4$ decreases the reactivity of $-\text{NH}_2$ groups, which makes the reaction between the lamellar $\text{g-C}_3\text{N}_4$ and the organic linker difficult under mild conditions [16]. To overcome the above obstacles, three dimensionally ordered macroporous (3DOM) $\text{g-C}_3\text{N}_4$ with interconnected macroporous architecture and large amounts of $-\text{NH}_2$ 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 $\text{g-C}_3\text{N}_4$. The hybrid catalyst of 3DOM $\text{g-C}_3\text{N}_4$ - 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_2O_2 for light-driven H_2O_2 production from H_2O and O_2 in the absence of organic electron donors.

2. Experimental section

2.1. Chemicals

Tetraethyl orthosilicate (TEOS), cyanamide, (triethoxysilyl)-propyl isocyanate, triethylamine, ammonium hydroxide solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%), hydrochloric acid (HCl, 37 wt%) and hydrofluoric acid (HF, 40 wt%) were purchased from Alfa Aesar company and used as received without further purification. 5,5-dimethyl-1-pyrroline (DMPO) were purchased from Sigma-Aldrich company. All solvents used were of analytical grade and were purchased from Fisher. Close-packed silica nanospheres [18] and $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}$ (K-PW_{11}) [19a] were synthesized and characterized in accordance with the literature.

2.2. Preparation of 3DOM $\text{g-C}_3\text{N}_4$ [17,20]

The powders of close-packed silica nanospheres (10.00g) and cyanamide (4.50g) were heated to 60 °C for 30 min to allow filling of the interparticle voids of close-packed silica nanospheres with molten cyanamide. The mixture of close-packed silica nanospheres and cyanamide was cooled to room temperature. After grinding, the mixture was put in a crucible with a lid and heated to 550 °C for 4 h in air. To remove the silica template, the mixture was soaked in 250 ml of 10 wt% HF aqueous solution for 1 day without stirring and the resulting solids were then recovered by centrifugation and washed with

water. Pale-yellow powders of 3DOM $\text{g-C}_3\text{N}_4$ were finally obtained by drying at 60 °C in air. Based on the TGA and EA analysis, the formula of 3DOM $\text{g-C}_3\text{N}_4$ was determined to be $\text{C}_{2.44}\text{N}_4\text{H}_{1.57}$. The lamellar $\text{g-C}_3\text{N}_4$ have been prepared without templates for comparison.

2.3. Preparation of 3DOM $\text{g-C}_3\text{N}_4$ - PW_{11}

3DOM $\text{g-C}_3\text{N}_4$ (1.00g) was dispersed in 50 ml acetonitrile and (triethoxysilyl)-propyl isocyanate (1.00g, 4.04 mmol) was added. The reaction mixture was kept at 80 °C, to which were added small amounts of triethylamine. After reaction for 24 h, the 3DOM $\text{g-C}_3\text{N}_4$ linker was obtained by centrifugation and used directly in the next step after washing with ethanol. Then, K-PW_{11} (6.40g, 2.02 mmol) was added to the 300 ml aqueous dispersion of 3DOM $\text{g-C}_3\text{N}_4$ linker. After adjusting the pH to 0.5 with 1 M HCl, the reaction mixture was stirred for 24 h. The hybrid catalyst of 3DOM $\text{g-C}_3\text{N}_4$ - PW_{11} was centrifugated, washed by water, and then dried at 60 °C in air. Based on the TGA, EA and ICP analysis, the formula of 3DOM $\text{g-C}_3\text{N}_4$ - PW_{11} was determined to be $\text{C}_{2.44}\text{N}_4\text{H}_{1.53}(\text{K}_3\text{PW}_{11}\text{O}_{42}\text{Si}_2\text{C}_8\text{H}_{14}\text{N}_2)_{0.021}$ (40.41 wt% PW_{11}). For comparison, 3DOM $\text{g-C}_3\text{N}_4$ - PW_{11} -IMP based on the electrostatic interaction has been prepared through the impregnation method with the same PW_{11} weight percentage as 3DOM $\text{g-C}_3\text{N}_4$ - PW_{11} based on covalent interaction.

2.4. Photocatalytic evaluation

The photocatalytic activities were evaluated by the activation of oxygen under light irradiation ($\lambda > 320\text{ nm}$) [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 (1 g 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_2O_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_2O_2 over the photocatalysts, a sample of 1 g L^{-1} was dispersed in H_2O_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 AFMSRXE 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 EtOH (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-1-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.

Fig. 1. Preparation process of 3DOM g-C₃N₄-PW₁₁.

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 covalently connect with 3DOM g-C₃N₄ linker under acidic solution following the reported method [19]. In this way, the POM cluster of PW₁₁ has been covalently 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 covalently 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(C=O)-, 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 covalently 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 covalently 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=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 indicate 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

Fig. 2. ¹³C (A), ²⁹Si (B) and ³¹P (C) MAS NMR spectra of 3DOM g-C₃N₄, K-PW₁₁ and 3DOM g-C₃N₄-PW₁₁.

covalent combination [15], indicating the decreased content of surface -NH_2 groups in 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$. CO_2 temperature programmed desorption ($\text{CO}_2\text{-TPD}$) has been performed to investigate the content of -NH_2 groups in 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ as the -NH_2 groups can act as Lewis base sites and adsorb slightly acidic CO_2 molecules [25]. Fig. S4 shows the peak area of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ is much smaller than that of 3DOM $\text{g-C}_3\text{N}_4$. Furthermore, the zeta potentials of aqueous suspension of 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ has been measured because the -NH_2 groups with the free lone pair electrons on nitrogen atoms can act as proton acceptors and acquire positive surface charges [26]. Fig. S5 shows the zeta potential of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ (-33.9 mV) is more negative than that of 3DOM $\text{g-C}_3\text{N}_4$ (-14.7 mV). The above IR, $\text{CO}_2\text{-TPD}$ and zeta potential results reveal the significant decrease of -NH_2 groups in 3DOM $\text{g-C}_3\text{N}_4$ after covalent combination, confirming the reaction between the -NH_2 groups of 3DOM $\text{g-C}_3\text{N}_4$ and the organosilicon linkers. The isotherms for 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ (Fig. S6A) are consistent with type II isotherm with a type H3 hysteresis loop in the relative pressure (P/P_0) 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 $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ possess clear macroporous structure [27]. The surface area, pore volume and pore diameter of 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ are shown in Table S1. Compared with 3DOM $\text{g-C}_3\text{N}_4$, the decrease in these values of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ is due to the covalent combination of PW_{11} cluster and the macroporous structure of 3DOM $\text{g-C}_3\text{N}_4$ [12a,d,d]. Thermogravimetry analysis (TGA) curves for 3DOM $\text{g-C}_3\text{N}_4$, K- PW_{11} and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ are shown in Fig. S7. The total weight loss of 3DOM $\text{g-C}_3\text{N}_4$ is 93.67% between 50 and 800 °C due to the direct thermal decomposition of 3DOM $\text{g-C}_3\text{N}_4$. For K- PW_{11} , 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 PW_{11} cluster for 3DOM $\text{g-C}_3\text{N}_4$ is 40.41%. Combining the TGA, EA and ICP analysis (Table S2), the molecular formulas of 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ can be given as $\text{C}_{2.44}\text{N}_4\text{H}_{1.57}$ and $\text{C}_{2.44}\text{N}_4\text{H}_{1.53}(\text{K}_3\text{PW}_{11}\text{O}_{42}\text{Si}_2\text{C}_8\text{H}_{14}\text{N}_2)_{0.021}$.

As shown in Fig. 3A, XPS peaks of C 1s for 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ 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 $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$. The tremendous increase of the C-C groups supports the organosilicon linker has been covalently linked with 3DOM $\text{g-C}_3\text{N}_4$. Nevertheless, the XPS peaks of N 1s (Fig. 3B) for 3DOM $\text{g-C}_3\text{N}_4$ 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 -NH_2 , respectively [8b]. However, the 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ only exhibits two peaks at 398.4 and 399.7 eV corresponding to N-(C₂) and N-(C₃). The disappearance of -NH_2 peak indicates that the -NH_2 groups of 3DOM $\text{g-C}_3\text{N}_4$ react with NCO- groups of silane coupling agent to form the carbamido groups during the covalent combination of PW_{11} cluster with 3DOM $\text{g-C}_3\text{N}_4$. The above C 1s and N 1s XPS results support the ^{13}C MAS NMR results of 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$. The XPS peak of Si 2p (Fig. 3C) for 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ shows one peak at 101.8 eV corresponding to R-Si-(O₃) (R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{C}=\text{O})-$), which is in accordance with ^{29}Si MAS NMR result of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ [28]. Both the 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ show one P 2p XPS peak at 133.3 eV (Fig. 3D). In addition, XPS peaks of W 4f (Fig. 3E) for K- PW_{11} and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ can be fitted with two peaks at binding energies of around 34.9 and 37.1 eV (W 4f_{7/2} and W 4f_{5/2}), which are consistent with a W(VI) oxidation state [13]. The P 2p and W 4f XPS results reveal that the primary structure of PW_{11} cluster has been well preserved after covalent combination. XPS peaks of O 1s (Fig. 3F) for K- PW_{11} and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ 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 W=O, respectively [12c]. The area ratios of these two peaks are 0.31 and 1.06 for K- PW_{11} and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$.

The largely increase of the W-O-O-W/Si supports the organosilicon linker are covalently tethered onto the vacancy of PW_{11} cluster. The above XPS results confirm the PW_{11} cluster has been covalently combined with 3DOM $\text{g-C}_3\text{N}_4$ through the organosilicon linker and the primary structure of PW_{11} cluster has been well preserved after covalent combination.

Fig. S8 are the TEM images of 3DOM $\text{g-C}_3\text{N}_4$ (Fig. S8A–C) and

Fig. 3. C 1s (A), N 1s (B), Si 2p (C), P 2p (D), W 4f (E), and O 1s (F) XPS spectra of 3DOM $\text{g-C}_3\text{N}_4$, K- PW_{11} and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$.

Fig. 4. STEM images (A and B) and corresponding elemental mappings (C–G) of 3DOM g-C₃N₄-PW₁₁.

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 ($\lambda \geq 320$ 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 $\mu\text{mol h}^{-1}$ 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 evaluates the rate constants for light-driven H₂O₂ formation and decomposition by assuming zero-order and first-order kinetics [31]:

$$[\text{H}_2\text{O}_2] = \frac{K_f}{K_d}(1 - e^{K_d t}) \quad (6)$$

The K_f and K_d values have been estimated by fitting the data in

Fig. 5. Light-driven H₂O₂ formation over different catalysts in 60 min. Reaction conditions: H₂O (100 ml), catalyst (0.10 g, 1 g L⁻¹), O₂-equilibrated, $\lambda \geq 320$ nm, 25 °C.

Fig. 6. Light-driven H_2O_2 decomposition over different catalysts. Reaction conditions: H_2O_2 solution (100 ml, initial concentration = 1 mM), catalyst (0.10 g, 1 g L^{-1}), $\lambda \geq 320 \text{ nm}$, 25°C .

Fig. 5A according to Eq. (6) and the results are presented in Fig. 5B. After the covalent combination of PW_{11} cluster with 3DOM $\text{g-C}_3\text{N}_4$, K_f value increases from 0.3090 to $0.7921 \mu\text{M min}^{-1}$ and K_d value decreases from 0.0123 to 0.0113 min^{-1} . The above results indicate that the covalent combination of PW_{11} and 3DOM $\text{g-C}_3\text{N}_4$ can enhance the H_2O_2 formation and stabilize the formed H_2O_2 under light irradiation.

The light-driven H_2O_2 decomposition over different catalysts has been conducted with an initial H_2O_2 concentration of 1 mM to investigate the decomposition behavior of H_2O_2 in the presence of catalysts. As shown in Fig. 6A, the H_2O_2 decomposes about 17% over 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ after 60 min, which is lower than those over 3DOM $\text{g-C}_3\text{N}_4$ (63%), K- PW_{11} (77%) and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}\text{-IMP}$ (83%). The H_2O_2 decomposes about 35% in the absence of catalyst. Owing to the large quantity of H_2O_2 (1 mM) and the constant amounts of the catalysts, the decomposition is expected to follow a pseudo-first-order reaction [32]:

$$-\frac{dc_t}{dt} = k_0 \quad (7)$$

where c_t is the H_2O_2 concentration at time t , k_0 is the pseudo-first-order rate constant, and c_0 is the initial concentration of H_2O_2 (1 mM) in this work. To more accurately evaluate the rate constants, we have fitted the decomposition data of different catalysts based on Eq. (7) and presented in Fig. 6B, where K_d is the first-order reaction rate constant. The results in Table S3 indicates that the values of K_d increases in the following order: 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ (0.0031 min^{-1}) < None (0.0073 min^{-1}) < 3DOM $\text{g-C}_3\text{N}_4$ (0.0167 min^{-1}) < K- PW_{11} (0.0243 min^{-1}) < 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}\text{-IMP}$ (0.0304 min^{-1}). An additional concern is that the formed H_2O_2 might react with PW_{11} cluster to form the Ishii-Venturello polyperoxometalate species of $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ [33]. The ^{31}P MAS NMR for used 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ (Fig. S11) shows no signal of these species, which rules out the formation of polyperoxometalate species during the light-driven H_2O_2 production [34]. The above results confirm that the covalent combination of PW_{11} and 3DOM $\text{g-C}_3\text{N}_4$ can stabilize the formed H_2O_2 under light irradiation.

It is important to note that under similar reaction conditions over the $\text{g-C}_3\text{N}_4$ -based catalysts in the absence of organic electron donors (Table 1), the H_2O_2 formation rate ($2.4 \mu\text{mol h}^{-1}$) over 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ is more than those over ($0.5 \mu\text{mol h}^{-1}$) $\text{g-C}_3\text{N}_4\text{-BDI}_{50}$ [35], ($1.0 \mu\text{mol h}^{-1}$) $\text{g-C}_3\text{N}_4\text{-PDI}_{51}$ [6b], ($1.2 \mu\text{mol h}^{-1}$) $\text{g-C}_3\text{N}_4\text{-PDI}_{51}\text{-rGOs}$ [6e], and ($1.8 \mu\text{mol h}^{-1}$) $\text{g-C}_3\text{N}_4\text{-NiFeO}$ [32], but inferior to that ($9.2 \mu\text{mol h}^{-1}$) over Cv- $\text{g-C}_3\text{N}_4$ [8b]. Though Cv- $\text{g-C}_3\text{N}_4$ shows better catalytic performance for two-electron O_2 reduction to H_2O_2 than 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$, the ability of water oxidation for Cv- $\text{g-C}_3\text{N}_4$ is negligible where H_2O_2 cannot be detected under Ar-equilibrated conditions [8b]. On the contrary, 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ can produce considerable amounts of H_2O_2 ($1.5 \mu\text{mol}$ in 60 min) under N_2 -equilibrated conditions (Fig. S12), indicating the 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ can act as a dual-functional catalyst for both water oxidation and oxygen reduction [32]. Nevertheless, the H_2O_2 formation rate ($2.4 \mu\text{mol h}^{-1}$)

Table 1

Comparison of the maximum formed H_2O_2 amounts (μmol) and H_2O_2 formation rate ($\mu\text{mol h}^{-1}$) over $\text{g-C}_3\text{N}_4$ -based photocatalyst.

Catalyst	Maximum formed H_2O_2 (μmol)	H_2O_2 Formation Rate ($\mu\text{mol h}^{-1}$)	Refs.
3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$	14.4	2.4	This work
$\text{g-C}_3\text{N}_4\text{-BDI}_{50}$ ^a	11.6	0.5	[35]
$\text{g-C}_3\text{N}_4\text{-PDI}_{51}$ ^b	50.6	1.0	[6b]
$\text{g-C}_3\text{N}_4\text{-PDI}_{51}\text{-rGOs}$ ^c	30.0	1.2	[6e]
$\text{g-C}_3\text{N}_4\text{-NiFeO}$	1.8	1.8	[32]
Cv- $\text{g-C}_3\text{N}_4$ ^d	9.2	9.2	[8b]

^a BDI=biphenyl diimide;

^b PDI=pyromellitic diimide;

^c rGOs=reduced graphene oxide;

^d Cv- $\text{g-C}_3\text{N}_4$ =carbon vacancy contained $\text{g-C}_3\text{N}_4$.

over 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ is more than those ($2.3 \mu\text{mol h}^{-1}$) over $\text{TiO}_2\text{-CoPi-rGOs}$ [6a] and ($0.5 \mu\text{mol h}^{-1}$) over CdS-rGOs_{20} [6f]. Therefore, the relative high H_2O_2 formation rate among the reported catalysts make 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ a promising catalyst for light-driven H_2O_2 production in the absence of organic electron donors.

3.4. Structure-catalytic performance relationship of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$

Photoelectrochemical characterization should be performed to clarify the reason for the efficient activity of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$. The catalysts of 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ 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. S13A, the photo-current density of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ ($0.43 \mu\text{A cm}^{-2}$) is much larger than that of 3DOM $\text{g-C}_3\text{N}_4$ ($0.01 \mu\text{A cm}^{-2}$). Photoelectrochemical impedance spectroscopy (EIS) results are shown in Fig. S13B. The diameter of Nyquist semicircle for 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ is smaller than that of 3DOM $\text{g-C}_3\text{N}_4$, which indicates that the 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ composites have lower resistances than 3DOM $\text{g-C}_3\text{N}_4$. The above results reveal that the covalent combination of PW_{11} and 3DOM $\text{g-C}_3\text{N}_4$ can enhance the charge separation of 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$. Photoluminescence (PL) spectrum has been used to explore the recombination and separation of photo-generated electrons and holes in the 3DOM $\text{g-C}_3\text{N}_4$ and 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ (Fig. S14A). The emission peak appearing at about 485 nm is attributed to the direct electron-hole recombination of band transition. Compare with 3DOM $\text{g-C}_3\text{N}_4$, 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ 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 PW_{11} cluster and 3DOM $\text{g-C}_3\text{N}_4$ can enhance charge separation and thus facilitate the light-driven formation of H_2O_2 . Furthermore, the above results also suggest that the 3DOM $\text{g-C}_3\text{N}_4\text{-PW}_{11}$ can act as a dual-functional catalyst for both water

Fig. 7. LSV curves of catalysts-loaded electrodes toward OER with scan rate of 10 mV s⁻¹ in the dark (A); DMPO spin trapping ESR technique to measure •OOH generated photoreaction over these catalysts (B); Koutecky-Levich plots of the ORR data measured by RDE analysis for 3DOM g-C₃N₄ or 3DOM g-C₃N₄-PW₁₁ (Fig. S13) in a buffered solution (pH 7) at a constant potential of -0.9 V vs Ag/AgCl (C); and scheme of energy levels and charge transfer pathways of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ (D).

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-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ in the dark. The onset potential of 3DOM g-C₃N₄ 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 (j) with bias (E) indicated a high kinetic barrier. In contrast, for 3DOM g-C₃N₄-PW₁₁, the onset potential negatively shifted to 1.63 V vs. NHE, and the current density was greatly enhanced compared to the 3DOM g-C₃N₄. The above results reveal that the OER performance of 3DOM g-C₃N₄-PW₁₁ is higher than that of 3DOM g-C₃N₄. ESR analysis with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping reagent has been performed to confirm the pathway of O₂ reduction over different catalysts. Fig. 7B shows the ESR spectrum of the solutions recovered after photoreaction over 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ for 3 min. Both solutions exhibit distinctive signals assigned to the DMPO-•OOH spin adduct ($a_N = 13.3$ G, $a_H^B = 10.1$ G, $g = 2.0065$) [8a]. The signal intensity for the solution obtained by photoreaction over 3DOM g-C₃N₄-PW₁₁ is much weaker than that over 3DOM g-C₃N₄. The results suggest that one-electron reduction of O₂ (Eq. (4)) is indeed suppressed over 3DOM g-C₃N₄-PW₁₁, and thus promotes the two-electron reduction of O₂ (Eq. (3)).

Electrochemical rotating disk electrode (RDE) analysis of oxygen reduction reaction (ORR) further investigates the pathway of O₂ reduction. Fig. S15 shows the LSV curves of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ measured on RDE in an O₂-saturated 0.1 M phosphate buffer solution (pH 7) at different rotating speeds. Fig. 7C summarizes the Koutecky-Levich plots of the data at -0.9 V vs. Ag/AgCl. The average number of electrons (n) involved in the overall O₂ reduction can be estimated by the linear regression of the plots using the following equations [36]:

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2} \quad (8)$$

$$B = 0.2nF\nu^{-1/6}CD^{2/3} \quad (9)$$

j is the current density, j_k is the kinetic current density, ω is the rotating speed (rpm), F is the Faraday constant (96485 C mol⁻¹), ν is the kinetic viscosity of water (0.01 cm² s⁻¹), C is the bulk concentration of O₂ in water (1.26 × 10⁻³ mol cm⁻³), and D is the diffusion coefficient of O₂ (2.7 × 10⁻⁵ cm² s⁻¹), respectively [37]. The n value for 3DOM g-C₃N₄ ($n = 1.85$) suggests that one-electron O₂ reduction indeed occurs, which confirms the ESR results. In contrast, 3DOM g-C₃N₄-PW₁₁ exhibits $n = 2.30$, indicating the covalent combination of 3DOM g-C₃N₄ and PW₁₁ can selectively promote the two-electron O₂ reduction. It has been reported that the enhanced O₂ adsorption of catalysts can promote the multi-electron reduction of O₂ [36,38]. Furthermore, O₂ temperature programmed desorption (O₂-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-C₃N₄-PW₁₁, indicating the amounts of O_{ads} in 3DOM g-C₃N₄-PW₁₁ are much more than those in 3DOM g-C₃N₄ and K-PW₁₁. Combining the ESR, Koutecky-Levich plots and O₂-TPD results, the enhanced O₂ adsorption of 3DOM g-C₃N₄-PW₁₁ can selectively promote the two-electron reduction of O₂ to H₂O₂.

The flat band potentials (E_{fb}) of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ 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]. A flat band potential of -0.15 V and 0.06 V vs. NHE has been obtained for 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁, respectively. The conduction band could be 0–0.1 V more negative than the flat band position. Hence, the corre-

Fig. 8. Experiment to prove the heterogeneous nature (A) and the recycle (B) of 3DOM g-C₃N₄-PW₁₁.

sponding CB edge of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ 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-C₃N₄ to 3DOM g-C₃N₄-PW₁₁ has been observed. The positive shift of the CB in 3DOM g-C₃N₄-PW₁₁ is likely to improve the selectivity of O₂ reduction to H₂O₂ [6e]. The Tauc plots of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ have been derived according to the relationship of $(F(R) \cdot h\nu)^2 = A(h\nu - E_g)$, where h is Planck's constant, ν 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-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ are 2.82 and 2.78 eV, respectively.

Combining the Mott-Schottky measurements and Tauc plots results, the VB positions of 3DOM g-C₃N₄ and 3DOM g-C₃N₄-PW₁₁ 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-C₃N₄-PW₁₁ are more positive than those of 3DOM g-C₃N₄. Because the water oxidation is a rate-limiting step, the positive shift of the VB in 3DOM g-C₃N₄-PW₁₁ facilitates to overcome the kinetic barrier of the O₂ evolution. Moreover, the CB level in 3DOM g-C₃N₄-PW₁₁ (−0.04 V vs. NHE) is more positive than the one-electron reduction of O₂ to •OOH (−0.13 V vs. NHE), and has sufficient potential difference (0.73 V) from the two-electron reduction of O₂ to H₂O₂ (0.69 V vs. NHE) [42]. The results are in accordance with the reported g-C₃N₄-PDI and g-C₃N₄-NiFeO catalysts, in which both the CB and VB levels of g-C₃N₄-PDI and g-C₃N₄-NiFeO are shifted positively [6e,32]. In these catalytic systems, the positive shifts of VB have proved to enhance the capability of 3DOM g-C₃N₄-PW₁₁ for water oxidation and promote the two-electron reduction of O₂ to H₂O₂.

3.5. Recycle of heterogeneous 3DOM g-C₃N₄-PW₁₁

It is essential to confirm the catalysis of 3DOM g-C₃N₄-PW₁₁ is truly heterogeneous for light-driven H₂O₂ production. When the reaction time arrives at 30 min, 3DOM g-C₃N₄-PW₁₁ 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 H₂O₂ forms and the formed H₂O₂ 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-C₃N₄-PW₁₁ is truly heterogeneous for H₂O₂ production.

To investigate the stability of heterogeneous 3DOM g-C₃N₄-PW₁₁, the light-driven production of H₂O₂ 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, ¹³C, ²⁹Si and ³¹P MAS NMR spectra of the fresh and used 3DOM g-C₃N₄-PW₁₁ exhibits almost the same typical peaks (Figs. S11, S18 and S19). The STEM-Mapping results of the used 3DOM g-C₃N₄-PW₁₁ (Fig. S20) indicates that the macroporous structure and the dispersion of PW₁₁ cluster on 3DOM g-C₃N₄ are

retained after reaction. The EA and ICP results in Table S2 also reveal that the composition of the used 3DOM g-C₃N₄-PW₁₁ remains unchanged. The above results indicate that the heterogeneous 3DOM g-C₃N₄-PW₁₁ is catalytic stable.

4. Conclusions

To summarize, the hybrid catalyst of 3DOM g-C₃N₄-PW₁₁ with well-defined and stable structure has been prepared by covalent combining the PW₁₁ cluster with 3DOM g-C₃N₄ through the organic linker strategy. The organosilicon agent of (triethoxysilyl)-propyl isocyanate can act as the linker to covalent combine the PW₁₁ cluster with 3DOM g-C₃N₄. The hybrid catalyst of 3DOM g-C₃N₄-PW₁₁ exhibits efficient catalytic performance for light-driven H₂O₂ production from H₂O and O₂ in the absence of organic electron donors. The catalytic and characterization results suggest the three reasons for the efficient catalytic performance of 3DOM g-C₃N₄-PW₁₁: 1) the covalent combination of PW₁₁ cluster and 3DOM g-C₃N₄ can enhance the charge separation of photogenerated holes and electrons; 2) the more positive potential of the valence band (VB) after the covalent combination can elevate photogenerated holes separation and involvement in water oxidation; 3) the conduction band (CB) level of 3DOM g-C₃N₄-PW₁₁ (−0.04 V vs. NHE) is more positive than that of the one-electron reduction of O₂ to •OOH (−0.13 V vs. NHE) and the potential difference between the CB level of 3DOM g-C₃N₄-PW₁₁ (−0.04 V vs. NHE) and O₂ to H₂O₂ potential (0.69 V vs. NHE) is sufficient (0.73 V), which can promote the two-electron reduction of O₂ to H₂O₂. In addition, the recycle experiment results reveal that the heterogeneous 3DOM g-C₃N₄-PW₁₁ is catalytic stable. The covalent combination of POMs and g-C₃N₄ 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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