



Polyoxometalates-derived metal oxides incorporated into graphitic carbon nitride framework for photocatalytic hydrogen peroxide production under visible light

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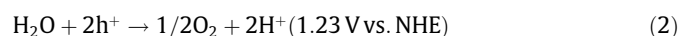
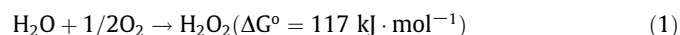
ABSTRACT

The hybrid catalyst of g-C₃N₄-PWO has been prepared through the calcination of the g-C₃N₄ precursor of dicyandiamide and the polyoxometalates (POMs) precursor of (NH₄)₃PW₁₂O₄₀ (NH₄-PW₁₂). The hybrid catalyst of g-C₃N₄-PWO with well-defined and stable structure exhibits efficient catalytic performance for photocatalytic H₂O₂ production in the absence of organic electron donor under visible light. The value of electron transfer during the oxygen reduction reaction (ORR) process obtained from the Koutecky-Levich plot for g-C₃N₄-PWO (n = 1.73) is higher than that for g-C₃N₄ (n = 1.29), suggesting that the PWO incorporated into g-C₃N₄ framework can promote the electrons generation. The *p*-benzoquinone (PBQ) scavenger experiments, the electron spin resonance (ESR) signal and quantitative experiment of superoxide radicals ([•]O₂⁻) results reveal that the negative shifts of the conduction band (CB) level from g-C₃N₄ to g-C₃N₄-PWO can enhance the single-electron reduction of O₂ to [•]O₂⁻ and further promote the sequential two-step single-electron O₂ reduction reaction to H₂O₂.

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1. Introduction

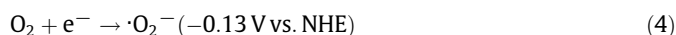
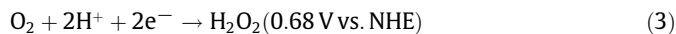
Hydrogen peroxide (H₂O₂) can be widely utilized in organic synthesis, environmental remediation, disinfection and one-compartment fuel cells alternative to hydrogen (H₂) because of its convenient and safe storage and transportation in liquid form and producing water (H₂O) as the sole byproduct [1]. However, the current H₂O₂ production methods have two disadvantages: (1) the anthraquinone method (the Riedl-Pfleiderer process) utilized in industry catalyzed by Pd-based catalysts requires the regeneration of anthrahydroquinone by H₂; [2a] 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 [2b]. Therefore, a noble metal-free approach capable of producing H₂O₂ without H₂ is highly desired.



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The photocatalytic H₂O₂ production method through proton-coupled electron transfer (PCET) process can meet the above requirement because it only needs H₂O, dioxygen (O₂) and light (Eq. (1) [3]). Among the semiconductor catalysts utilized in the photocatalytic H₂O₂ production, graphitic carbon nitride (g-C₃N₄)-based catalysts exhibit good efficiency for photocatalytic H₂O₂ production because the formed 1,4-endoperoxide species on the g-C₃N₄ surface actually gets transformed as H₂O₂ molecule [4]. However, the low valence band (VB) potential of g-C₃N₄ is insufficient for water oxidation because of the small thermodynamic driving force (Eq. (2) [5]). Two approaches that using the organic electron donor in the reaction system [6] and shifting the VB potential of g-C₃N₄-based catalysts more positively [7] have been adopted to solve the above problem. Generally, the photocatalytic H₂O₂ production over g-C₃N₄-based catalysts can process either a direct two-electron O₂ reduction (Eq. (3) [7] or a sequential two-step single-electron O₂ reduction (Eqs. (4) and (5) [8]). Rather than using the above approaches, making use of the photoredox activity of g-C₃N₄ and shifting the conduction band (CB) potential of g-C₃N₄-based catalysts more negatively is a new attempt. Negatively shifting the CB potential of g-C₃N₄-based catalysts can enhance the one-electron reduction of O₂ to superoxide radicals ([•]O₂⁻) and further promote the sequential two-step single-electron O₂ reduction reaction to H₂O₂ [9].



During photocatalysis process, the electron transfer materials such as the metal complex and carbonaceous nanomaterials immobilized onto $g\text{-C}_3\text{N}_4$ can accept the photoinduced electrons from the CB level of $g\text{-C}_3\text{N}_4$ and increase the efficiency of reduction reaction [10]. As efficient electrocatalysts for hydrogen evolution reaction (HER) and overall water splitting, the polyoxometalates (POMs)-derived metal oxides are capable of accepting, transporting and storing electrons [11]. Therefore, introducing the POMs-derived metal oxides in $g\text{-C}_3\text{N}_4$ to form the hybrid catalysts can enhance the photoinduced electrons generation and further increase the activity of reduction reaction. Herein, the hybrid catalyst of $g\text{-C}_3\text{N}_4\text{-PWO}$ has been prepared through the calcination of the $g\text{-C}_3\text{N}_4$ precursor of dicyandiamide and the POMs precursor of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ ($\text{NH}_4\text{-PW}_{12}$). The hybrid catalyst of $g\text{-C}_3\text{N}_4\text{-PWO}$ with well-defined and stable structure exhibits efficient catalytic performance for photocatalytic H_2O_2 production in the absence of organic electron donor under visible light. The catalytic and characterization results reveal that the incorporation of PWO into $g\text{-C}_3\text{N}_4$ framework can enhance the single-electron reduction of O_2 to $\cdot\text{O}_2^-$ and further promote the sequential two-step single-electron O_2 reduction reaction to H_2O_2 .

2. Experimental section

2.1. Chemicals

Dicyandiamide, ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), ammonium metatungstate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$), nitro blue tetrazolium (NBT) were purchased from Alfa Aesar company and used as received without further purification. 5,5-dimethyl-1-pyrroline (DMPO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were purchased from Sigma-Aldrich company. $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ ($\text{NH}_4\text{-PW}_{12}$) [12] were synthesized and characterized in accordance with the literature.

2.2. Preparation of $g\text{-C}_3\text{N}_4$ [13]

Dicyandiamide (6.00 g, 0.07 mol) was placed in a quartz boat and heated under N_2 flow at 550°C for 4 h at a rate of $3^\circ\text{C}\cdot\text{min}^{-1}$. Then, the quartz boat was cooled to room temperature naturally. The obtained product was collected and ground into fine powder for further use. Based on the EA analysis, the formula of $g\text{-C}_3\text{N}_4$ was determined to be $\text{C}_{2.31}\text{N}_4\text{H}_{1.98}\text{O}_{0.74}$.

2.3. Preparation of PWO

$\text{NH}_4\text{-PW}_{12}$ (6.00 g, 2.02 mmol) was placed in a quartz boat and heated under N_2 flow at 550°C for 4 h at a rate of $3^\circ\text{C}\cdot\text{min}^{-1}$. Then, the quartz boat was cooled to room temperature naturally. The obtained product was collected and ground into fine powder for further use. Based on the EA and ICP analysis, the formula of PWO was determined to be $\text{P}_{0.99}\text{W}_{12.01}\text{O}_{40.03}$.

2.4. Preparation of $g\text{-C}_3\text{N}_4\text{-PWO}$

Dicyandiamide (4.00 g, 0.05 mol) and $\text{NH}_4\text{-PW}_{12}$ (2.00 g, 0.67 mmol) were completely mixed in deionized water and kept stirring for 24 h, and then allowed to remove water at 90°C . Then the precursors were placed in a quartz boat and heated under N_2 flow at 550°C for 4 h at a rate of $3^\circ\text{C}\cdot\text{min}^{-1}$. Then, the quartz boat was

cooled to room temperature naturally. The obtained product was collected and ground into fine powder for further use. Based on the EA and ICP analysis, the formula of $g\text{-C}_3\text{N}_4\text{-PWO}$ was determined to be $\text{C}_{2.30}\text{N}_4\text{H}_{1.96}\text{P}_{0.03}\text{W}_{0.38}\text{O}_{2.02}$. For comparison, $g\text{-C}_3\text{N}_4\text{-P}$ and $g\text{-C}_3\text{N}_4\text{-WO}$ have been prepared through the same method with the same molar of P ($\text{NH}_4\text{H}_2\text{PO}_4$ as precursor) or W ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ as precursor) as $g\text{-C}_3\text{N}_4\text{-PWO}$. Based on the EA and ICP analysis, the formula of $g\text{-C}_3\text{N}_4\text{-P}$ and $g\text{-C}_3\text{N}_4\text{-WO}$ were determined to be $\text{C}_{2.30}\text{N}_4\text{H}_{1.96}\text{P}_{0.03}\text{O}_{0.82}$ and $\text{C}_{2.30}\text{N}_4\text{H}_{1.96}\text{W}_{0.38}\text{O}_{2.02}$, respectively.

2.5. Photocatalytic evaluation

The photocatalytic activities were evaluated by the activation of oxygen under light irradiation ($\lambda \geq 420 \text{ nm}$). A 300 W Xenon lamp (Perfect Light Company, Beijing) was chosen as light source. During each photocatalytic performance, 0.10 g of catalyst was dispersed into 100 ml of water in a container ($1 \text{ g}\cdot\text{L}^{-1}$ 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, 1.50 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 [14]. 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 catalyst of $1 \text{ g}\cdot\text{L}^{-1}$ was dispersed in H_2O_2 solution (initial concentration: 1 mM) and irradiated for 60 min under continuous stirring.

3. Results and discussion

3.1. Preparation of $g\text{-C}_3\text{N}_4\text{-PWO}$

As shown in Fig. 1, the hybrid catalyst of $g\text{-C}_3\text{N}_4\text{-PWO}$ has been prepared through the calcination of the $g\text{-C}_3\text{N}_4$ precursor of dicyandiamide and the POMs precursor of $\text{NH}_4\text{-PW}_{12}$. The XRD patterns of $\text{NH}_4\text{-PW}_{12}$, PWO, $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4\text{-P}$, $g\text{-C}_3\text{N}_4\text{-WO}$ and $g\text{-C}_3\text{N}_4\text{-PWO}$ are shown in Fig. S1A. The $\text{NH}_4\text{-PW}_{12}$ possesses the typical peaks of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ cluster [12]. The $\text{NH}_4\text{-PW}_{12}$ has been completely transformed to the $\text{W}_{12}\text{PO}_{38.5}$ (JCPDS 41-0369) phase after calcination [15]. The $g\text{-C}_3\text{N}_4$ has two distinct diffraction peaks at 13.1° and 27.6° , which correspond to the graphitic materials as the (1 0 0) and (0 0 2) diffraction planes in JCPDS 87-1526 [16]. For $g\text{-C}_3\text{N}_4\text{-PWO}$, the peaks intensities at 13.0 and 27.5° decreases compared with $g\text{-C}_3\text{N}_4$ (Fig. S1A), which indicates that the polymeric structure of $g\text{-C}_3\text{N}_4\text{-PWO}$ is possibly derived from the simultaneous condensation of melamine and $\text{NH}_4\text{-PW}_{12}$. In the case of dicyandiamide (Fig. S1B), melamine-based products are dominant at 350°C , but *tri-s*-triazine (melem) starts to generate as a result

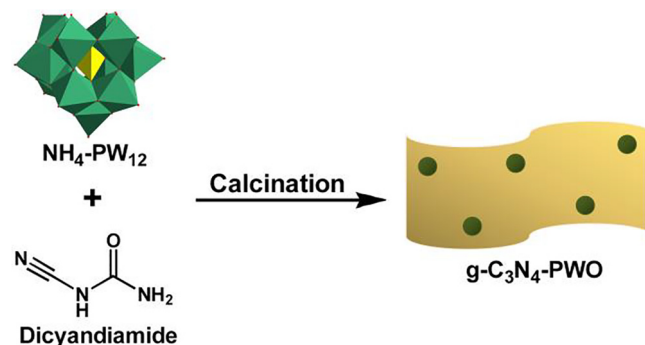


Fig. 1. Preparation process of $g\text{-C}_3\text{N}_4\text{-PWO}$.

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