Facile Synthesis of Lacunary Keggin-Type Phosphotungstates-Decorated g-C_3N_4 Nanosheets for Enhancing Photocatalytic H_2 Generation

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Abstract: In this work, the lacunary Keggin-type phosphotungstates of [PW_9O_34]^{9-} (PW_9) clusters were loaded onto the g-C_3N_4 nanosheets (NSs) to synthesize the phosphotungstate clusters-decorated 2D heterojunction photocatalysts by using the electrostatic-force driven self-assembly process. The surface charge polarity of g-C_3N_4 NSs was changed from a negative to a positive charge through the acidizing treatment. The positively-charged g-C_3N_4 NSs allowed the negatively-charged PW_9 clusters to be adsorbed and deposited onto the g-C_3N_4 NSs, forming the PW_9/g-C_3N_4 heterojunction NSs. The as-synthesized samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, and UV-VIS absorption spectra, respectively. The photocatalytic activity tests indicated that, upon simulated sunlight irradiation, the photocatalytic H_2-generation rate of PW_9/g-C_3N_4 heterojunction NSs (~23.8 µmol h^{-1}) was ~3.3 times higher than that of the pure g-C_3N_4 NSs (~7.3 µmol h^{-1}). The enhanced photocatalytic activity of PW_9 cluster-decorated g-C_3N_4 NSs could be attributed to the enhanced separation process of the photoinduced charge-carriers, due to the Z-scheme-mediate charge transfer behavior across their hetero-interface.  

Keywords: photocatalysis; g-C_3N_4; H_2 generation; Z-scheme mechanism; electron transfer

1. Introduction  

The continuous burning of unsustainable fossil energy sources, which emits large amounts of harmful gases, has induced a global energy crisis and environmental contamination. The development of green renewable energy sources to replace traditional fossil energy sources has become an urgent issue [1,2]. As a kind of pollution-free sustainable fuel, hydrogen (H_2) has been regarded as an ideal candidate for the application of energy supply in future society [3,4]. Splitting water through the additional electric or photic energy is a common method to obtain the H_2. Since the H_2 generation from the photo-driven water splitting over the TiO_2 semiconductor photocatalyst was first reported in 1972 [5], this photochemical reaction has been widely used in the research area of solar-to-fuels conversion, mainly owing to its low cost and low energy consumption [6–8]. However, because the classical photocatalyst of TiO_2 nanostructures is a wide bandgap semiconductor (3.0–3.2 eV), it can only absorb the UV light that accounts for 3–5% in the solar spectrum [9,10]. Thus, the development of narrow bandgap semiconductors as the photocatalysts for H_2 generation has emerged as a hot topic in the area of solar-to-fuels conversion.
As a polymeric semiconductor made of carbon and nitrogen elements, graphite C₃N₄ (g-C₃N₄) material has attracted increasing interest in the area of photocatalytic H₂ generation [11,12]. This kind of metal-free semiconductor with a 2D nanosheet structure can open new prospects for the application of solar-to-fuels conversion because it is an abundant, cheap and stable semiconductor, with a suitable energy-level position for reducing protons. However, the fast recombination of the photoinduced charge-carriers often results in poor photocatalytic activity of the g-C₃N₄ NSs [13]. To overcome this problem, much effort has been contributed to couple the g-C₃N₄ NSs with an appropriate photoactive material to construct the 2D heterojunction photocatalyst toward high-efficient photocatalytic H₂ generation.

As a class of polyoxometalates, lacunary Keggin-type phosphotungstates have been extensively investigated as photosensitizers for enhancing the photocatalytic activity of the semiconductor photocatalysts for H₂O₂ production, H₂ generation, CO₂ reduction, pollution degradation, and organic material synthesis [14–16]. Similar to the inorganic semiconductors, the phosphotungstates also have the photoinduced electron transition behavior from the HOMO (Highest Occupied Molecular Orbital) to LUMO (Lowest Unoccupied Molecular Orbital). In general, the charge-transfer from the ligand to metal (O to W) in the phosphotungstates enable them to possess a high light absorption coefficient. Meanwhile, the enriched metal nodes of such W in the phosphotungstates can boost the photoinduced multi-electron redox-processes for fulfilling the various photo-chemical reactions [17]. Furthermore, when the lacunary Keggin-type phosphotungstates are dissolved in a water solution, the negatively-charged phosphotungstates can be obtained due to the ionization effect, thereby leading the phosphotungstates to be easily absorbed onto the substrate with the positive charge [18,19]. Notably, the surface charge polarity of g-C₃N₄ NSs is controllable by the acidizing treatment. It is concluded that the lacunary Keggin-type phosphotungstates are one of the ideal guest photosensitizers for coupling with the g-C₃N₄ NSs host, through the electrostatic-force driven self-assembly process for enhancing the photocatalytic H₂ generation of g-C₃N₄ NSs.

In this work, we adjusted the surface charge polarity of g-C₃N₄ to positive by using the acidizing treatment, and loaded the lacunary Keggin-type phosphotungstates of [PW₉O₃₄]⁹⁺ (PW₉) clusters onto the g-C₃N₄ NSs, forming the PW₉/g-C₃N₄ heterojunction NSs, via a facile self-assembly process due to the electrostatic interaction. We expected to utilize the photoinduced electrons on the LUMO of PW₉ component transfer to the valence band (VB) of g-C₃N₄ component for extending the lifetime of photoinduced electrons on the conduction band (CB) of g-C₃N₄ for executing protons reduction and improving the photocatalytic activity of the PW₉/g-C₃N₄ heterojunction NSs for H₂ generation. It is believed that our work will provide a new platform to construct the ultra-small polyoxometalates cluster-decorated g-C₃N₄ NSs for highly-efficient photocatalytic solar-to-fuels conversion.

2. Experimental

2.1. Synthesis of the PW₉, g-C₃N₄ NS, and PW₉/g-C₃N₄ Heterojunction NSs

The lacunary Keggin-type phosphotungstates of Naₙ[A-α-PW₉O₃₄]·7H₂O (named as PW₉) were synthesized by using the previously reported method [20]. The g-C₃N₄ was synthesized through the traditional thermal polymerization method by using the urea as the precursor [21]. To obtain the PW₉/g-C₃N₄ heterojunction NSs, 100 mg of the g-C₃N₄ bulk was ground and then dispersed into deionized water under the ultrasonic treatment for 90 min at room temperature, thereby achieving the g-C₃N₄ nanosheets (NSs). Afterward, 1 M of HCl solution was added dropwise into the above g-C₃N₄ nanosheets-suspended water solution to adjust the surface charge polarity of the NSs. After that, 100 mg of the PW₉ was dissolved into the above solution with vigorous stirring for 4 h. The precipitate in the solution was separated by centrifugation treatment. Finally, the obtained mixture was dried at 80 °C for 12 h, which was then under annealing at 300 °C for 2 h in vacuum. Thus, the PW₉/g-C₃N₄ heterojunction NSs were synthesized.
2.2. Characterization

The structure and morphology of the as-synthesized samples were observed by scanning electron microscopy (Field Emission-SEM; S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2100, JEOL, Tokyo, Japan). The X-ray diffraction (XRD) patterns of the as-fabricated samples were studied by X-ray diffractometer (XRD-6000, Shimadzu, Tokyo, Japan) with a Cu Kα line of 0.1541 nm and the radiation is from 10° to 65° at a scanning rate at 2°/min. The Fourier-transform infrared (FTIR) spectra were recorded on Magna 560 FTIR spectrometer (Thermo Nicolet Corporation, Madison, WI, USA) with a resolution of 1 cm⁻¹. The UV-VIS absorption spectra of the samples were recorded on a Lambda 750 UV/VIS/NIR spectrophotometer (Perkin Elmer, Waltham, MA, USA). The specific surface areas of the as-prepared samples were measured with a Micromeritics ASAP-2020 instrument (USA), and analyzed by the Brunauer–Emmett–Teller (BET) method. The surface charge polarity of the samples was measured with a dynamic light scattering spectrophotometer and isoelectric point determination with zeta potential analysis (SZ-100, Horiba, Tokyo, Japan).

2.3. Photocatalytic H₂ Generation

Five milligrams of the as-synthesized samples were dispersed into 10 mL of a water solution containing triethanolamine (TEOA, 15 vol.%) and chloroplatinic acid (H₂PtCl₆, 10 µL, 12 mM). Then, the mixture solution was sealed in a quartz reactor and then ventilated with argon gas for 10 min to drive away the residual air. Afterward, the reactor was exposed under simulated sunlight (300-W Xe lamp, PLS-SXE300UV, Beijing, China, coupled with an AM 1.5 filter, the wavelength range of light was from 320–2500 nm, the light density was 100 mW cm⁻², and the photon flux of the lamp was 0.17 µmol s⁻¹ m⁻²). The produced gas was periodically analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (Beifen-Ruili Analytical Instrument, SP-3420A, Beijing, China).

3. Results and Discussion

To synthesize the PW₉/g-C₃N₄ heterojunction NSs, the g-C₃N₄ bulk was crushed into the g-C₃N₄ nanosheets (NSs), at first, through the ultrasonic method. Then the obtained g-C₃N₄ NSs underwent the acidizing treatment to adjust their surface charge polarity from −21 mV to +6.6 mV. Afterward, the positively-charged g-C₃N₄ NSs were suspended into the water solution of PW₉ to enable the negatively-charged PW₉ to be self-assembled onto the g-C₃N₄ NSs, based on the electrostatic force [22,23]. Finally, the target sample of PW₉/g-C₃N₄ heterojunction NSs was synthesized for further investigation. Figure 1B shows the scanning electron microscopy (SEM) image of the pure g-C₃N₄ NSs. It can be seen that the sheet-like g-C₃N₄ has a relatively smooth surface. After PW₉ loading, there was also no change on the surface roughness of the g-C₃N₄ NSs in the PW₉/g-C₃N₄ composite NSs (Figure 1C). In order to further investigate the as-prepared PW₉/g-C₃N₄ heterojunction NSs, the high-resolution transmission electron microscopy (HRTEM) and the dark-filed scanning mode TEM were carried out. Although the lattice-fringe spacing of both PW₉ and g-C₃N₄ cannot be observed in HRTEM (Figure 1D), further investigation, by using dark-filed scanning mode TEM (STEM), indicated that the PW₉ clusters with sizes of 3–5 nm were decorated on the surface of g-C₃N₄ NSs in their heterojunction NSs (Figure 1E). In addition, the specific surface areas of PW₉/g-C₃N₄ heterojunction NSs (~68.7 m²/g) was similar to that of g-C₃N₄ (~53.1 m²/g), as shown in Figure S1.
The phase structures of the as-synthesized samples were identified through X-ray diffraction (XRD) patterns. As shown in Figure 2, the two intense diffraction peaks around 28°~30° can be observed on the XRD pattern of the PW9, which is in accordance with the feature peaks of the PW9 reported in the literature [24]. Meanwhile, the other peaks on the diffraction pattern of the Na-PW9 were also matched with that of the reported PW9, confirming the obtained lacunary Keggin-type phosphotungstates of PW9. In the case of g-C3N4 NSs, the two feature diffraction peaks, belonging to the periodic structure of intra-planar tri-s-triazine and the interlayer stacking of conjugated aromatic structures of g-C3N4 NSs were found at 13.1° and 27.4°, respectively [25–28]. This is in agreement with the graphite structure of carbon nitride. When the modification of g-C3N4 NSs with PW9 clusters took place, the feature peaks originated from the Na-PW9 with the center at 29.3° and the g-C3N4 NSs with centers at 13.1° and 27.4° and appeared on the XRD pattern of the formed composite. This result suggests that the g-C3N4 NSs were decorated with the lacunary Keggin-type phosphotungstates of PW9 clusters.
To further confirm the existence of the PW$_9$ clusters on the g-C$_3$N$_4$ NSs, the Fourier-transform infrared (FTIR) spectra of the PW$_9$/g-C$_3$N$_4$ heterojunction NSs along with the corresponding single hetero-components were tested, as shown in Figure 3. For the pure PW$_9$, the classical stretching vibrations related to the W-O-W, W-O, and P-O bonds were positioned around the 804/890, 984, and 1077 cm$^{-1}$, respectively [29,30]. It further proves the formation of lacunary Keggin-type phosphotungstates of PW$_9$. In the case of pure g-C$_3$N$_4$ NSs, the vibration bands between 1200 and 1650 cm$^{-1}$ were ascribed to the CN heterocycles [24,31]. The band at 811 cm$^{-1}$ is attributed to the feature vibration mode of s-triazine ring unit [32]. These observations are consistent with the literatures. The feature stretching vibration bands of both PW$_9$ and g-C$_3$N$_4$ could be found on the FTIR spectrum of the PW$_9$/g-C$_3$N$_4$ heterojunction NSs, powerfully confirming the successful decoration of the PW$_9$ clusters onto the g-C$_3$N$_4$ NSs. Notably, as compared with pure g-C$_3$N$_4$, the feature band at 811 cm$^{-1}$ was slightly shifted to 809 cm$^{-1}$, which might be the cause of the chemical interaction between PW$_9$ and g-C$_3$N$_4$ produced by the electrostatic adsorption process.

![Figure 3. FTIR spectra of the as-synthesized samples: (a) PW$_9$; (b) PW$_9$/g-C$_3$N$_4$ heterojunction NSs; (c) g-C$_3$N$_4$ NSs.](image)

The light absorption behaviors of the as-synthesized samples were evaluated through UV-VIS absorption spectra. As observed in Figure 4, the absorption edge of the pure PW$_9$ is located around 350 nm, corresponding to the forbidden gap of ~3.5 eV between HOMO and LUMO of the PW$_9$ [15,33]. Meanwhile, the absorption edge of pure g-C$_3$N$_4$ NSs appears at ~480 nm, suggesting the ~2.6 eV of the bandgap of the g-C$_3$N$_4$ NSs [34]. The above results indicate that the PW$_9$ and g-C$_3$N$_4$ NSs are the UV and visible absorbers, respectively, during the photo-excitation process. After loading the PW$_9$ clusters onto the surface of g-C$_3$N$_4$ NSs, the formed PW$_9$/g-C$_3$N$_4$ heterojunction NSs displayed the blue-shift behavior of the absorption edge, due to the introduction of the UV-light-active PW$_9$ hetero-component. By combining the results of the SEM, TEM, XRD, FTIR, and UV-VIS absorption spectra, we confirm that the PW$_9$/g-C$_3$N$_4$ heterojunction NSs with a well-distribution of PW$_9$ clusters were successfully synthesized by using the self-assembly process driven by the electrostatic force.
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Photocatalytic activity of the as-synthesized PW9/g-C3N4 heterojunction NSs for H2 generation was assessed under simulated sunlight excitation in the presence of the sacrificial agent of triethanolamine (TEOA) to quench the photoinduced hole. As observed in Figure 5A, there is no observable H2 generation under simulated sunlight irradiation for 2 h, when using the single PW9 as the photocatalyst. Meanwhile, the pure g-C3N4 NSs only displayed a poor photocatalytic activity for H2 generation (~14.6 µmol in 2 h-irradiation). After self-assembling the PW9 clusters onto the g-C3N4 NSs to form the PW9/g-C3N4 heterojunction NSs, the photocatalytic activity of the heterojunction NSs for H2 generation remarkably increased to ~47.6 µmol in 2 h-irradiation. The H2 generation rate of the PW9/g-C3N4 heterojunction NSs was 3.3 times higher than that of the g-C3N4 NSs, as summarized in Figure 5B. Notably, this photocatalytic activity is almost the highest one among the values reported for other g-C3N4-based photocatalytic systems (Table 1). Moreover, the solar-to-hydrogen (STH) efficiency has become an important index for evaluating the photocatalytic activity of hydrogen production. The STH efficiency under simulated sunlight irradiation can be calculated according to the following equation [35,36]:

\[
\text{STH} = \frac{\text{Energy of generation of hydrogen by water splitting}}{\text{Solar energy irradiating the reaction cell}} \times 100\%
\]  

After calculating, the STH of PW9/g-C3N4 heterojunction NSs was determined to be about 0.26% at room temperature.

It should be pointed out that the LUMO potential of PW9 does not satisfy the demand of proton reduction, while the g-C3N4 possesses a suitable conduction band (CB) potential for fulfilling the H2 generation [37,38]. Thus, we could deduce that the photocatalytic sites in the PW9/g-C3N4 heterojunction NSs should be located at the surface of g-C3N4 hetero-component [39,40]. Meanwhile, the PW9 hetero-component serves as the photosensitizer to boost the separation process of the photoinduced charge-carriers of the g-C3N4 hetero-component. According to the energy band structures of the reported Keggin-type phosphotungstate and g-C3N4 NSs, the LUMO position is a little higher than that of the g-C3N4 NSs, but it is still lower than the valence band (VB) position of the g-C3N4 NSs, as illustrated in the inset of Figure 5B. Thus, when the PW9/g-C3N4 heterojunction NSs is excited by simulated sunlight that contains the photon energies in both UV and visible light regions, the photoinduced electron-hole pairs are generated on the CB and VB of the PW9 and g-C3N4 hetero-components, respectively [41,42]. Owing to the potential difference between the LUMO of PW9 and the VB of g-C3N4, the photoinduced electrons on the LUMO of PW9 could transfer to the VB of g-C3N4 in the heterojunction NSs, thereby extending the lifetimes of the photoinduced electrons on the CB of g-C3N4 for implementing the photocatalytic H2 generation 

Figure 4. UV-VIS absorption spectra of the as-synthesized samples: (a) PW9; (b) PW9/g-C3N4 heterojunction NSs; (c) g-C3N4 NSs; the inset were plots of the [F(R)(hν)]1/2 versus hν of (a) PW9; (c) g-C3N4 NSs.
In this way, the Z-scheme photocatalytic mechanism can be employed to explain the enhanced photocatalytic activity of the PW$_9$/g-C$_3$N$_4$ heterojunction system.

![Figure 5](image_url)

**Figure 5.** (A) Time-dependent photocatalytic H$_2$-generation plots over the different samples under simulated sunlight irradiation: (a) PW$_9$; (b) g-C$_3$N$_4$ NSs; (c) PW$_9$/g-C$_3$N$_4$ heterojunction NSs; (B) H$_2$-generation rates of the PW$_9$/g-C$_3$N$_4$ heterojunction and g-C$_3$N$_4$ NSs.

| Catalyst                  | Precursor | Light Source                        | Activity   | Ref.    |
|---------------------------|-----------|-------------------------------------|------------|---------|
| Ag/g-C$_3$N$_4$/TiO$_2$   | Melamine  | 300 W Xe lamp with AM 1.5 filter    | 1.5 µmol/h | [44]    |
| W$_{18}$O$_{49}$/g-C$_3$N$_4$ | Urea     | 300 W Xe lamp with λ > 420 nm filter | 3.69 µmol/h | [45]    |
| g-C$_3$N$_4$/MnO$_2$      | Urea     | 300 W Xe lamp with λ > 420 nm filter | 5.53 µmol/h | [46]    |
| ZnIn$_2$S$_4$/g-C$_3$N$_4$ | Melamine | 300 W Xe lamp with λ > 420 nm filter | 14.1 µmol/h | [47]    |
| W$_{18}$O$_{49}$/g-C$_3$N$_4$ | Melamine | 300 W Xe lamp with λ > 420 nm filter | 18.25 µmol/h | [48]    |
| Zn-In$_2$S$_3$/g-C$_3$N$_4$ | Urea     | 300 W Xe lamp with λ > 420 nm filter | 17.32 µmol/h | [49]    |
| MoS$_2$/g-C$_3$N$_4$      | Urea     | 300 W Xe lamp with λ > 420 nm filter | 19.66 µmol/h | [50]    |
| PW$_9$/g-C$_3$N$_4$       | Urea     | 300 W Xe lamp with AM 1.5 filter    | 23.8 µmol/h | This work |

If the Z-scheme electron-transfer process is the main factor for enhancing the photocatalytic activity of PW$_9$/g-C$_3$N$_4$ heterojunction NSs, the hetero-interface combination force between these two hetero-components should have an influence on the photocatalytic H$_2$ generation of the NSs. In order to investigate this hypothesis, we synthesized another heterojunction NSs of g-C$_3$N$_4$, decorated with the normal Keggin-type phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$) (PW$_{12}$). Because the number of the negative charges in PW$_{12}$ is less than that in PW$_9$ when dissolving them in water solution, the combination force between the PW$_{12}$ and g-C$_3$N$_4$ should be lower than that in the PW$_9$ and g-C$_3$N$_4$ system. In theory, a strong combination force between the hetero-components would build a high-quality of the transport channel for electron transfer between the hetero-components [51,52]. Thus, the interfacial electron transfer process in the PW$_9$/g-C$_3$N$_4$ heterojunction NSs should be more effective for driving the Z-scheme photocatalytic H$_2$ generation as compared to the PW$_{12}$/g-C$_3$N$_4$ heterojunction NSs (the insets of Figure 6) [53]. The comparison study of the photocatalytic activities of the above two heterojunction NSs indicated that the H$_2$-generation activity of PW$_9$/g-C$_3$N$_4$ heterojunction NSs (~47.6 µmol in 2 h irradiation) was ~1.3 times higher than that of the PW$_{12}$/g-C$_3$N$_4$ heterojunction NSs (~35.3 µmol in 2 h irradiation). This evidence further confirms a fast Z-scheme charge-transfer process occurred in the intimate hetero-interface of PW$_9$/g-C$_3$N$_4$ for enhancing the photocatalytic H$_2$ generation.
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