

Intercalating Visible-Light-Responsive Polyoxotungstate Catalyst into Silicate Nanochannels of Arrayed Co-catalytic Platinum Nanoparticles for Highly Efficient Photocatalytic Hydrogen Production

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Abstract

The use of visible-light-responsive catalysts in hydrogen production is of increasingly higher interest owing to deteriorating energy and environment resources. Here, we present a highly efficient system for photocatalytic hydrogen production, comprising a novel visible-light-responsive polyoxotungstate (PTA) catalyst embedded along the walls of ordered silicate nanochannels of arrayed co-catalytic platinum nanoparticles within. The UV-visible-light-responsive PTA catalyst is synthesized by replacing a corner WO^{4+} of PTA with Ni for Ni- ℓ PTA, and then embedded to the walls of ordered silicate channels during synthesis of the MCM41-based template at an air-liquid interface. The silicate channel template with Ni- ℓ PTA (Ni- ℓ PMS) assists subsequent formation of arrays of densely packed Pt nanoparticles within the silicate channels upon UV light irradiation, via anion exchange of the Pt-metal precursors and the surfactant micelles. The hence formed nanocomposite of closely packed catalytic pairs of Ni- ℓ PTA and Pt nanoparticles along the 2D hexagonally ordered silicate nanochannels, demonstrates highly elevated hydrogen production upon AM1.5 sunlight illumination, compared to systems with PTA alone or with randomly dispersed Pt nanoparticles. With in situ grazing incidence small-angle X-ray scattering (GISAXS) on the air-liquid interface, formations of the ordered and oriented silicatropic template and the subsequent formation of Pt NP arrays in the PTA template are traced.

Keywords: *UV-Visible-Light-Responsive PTA, Arrayed Pt nanoparticles, Photocatalytic hydrogen production, meso-ordered silicatropic template, grazing incidence small-angle X-ray scattering*

Introduction

Photocatalytic hydrogen production, as a clean non-carbon energy source, has a great potential to solve the crisis of energy shortage and excessive emissions of global warming gases. Polyoxometalate (POM) is nanoscale metal oxygen anionic clusters (0.6-2.5nm), which exhibit remarkably fast and reversible multi-electron redox, well-thermal stability and optical properties, can be widely used in catalysis, electrical devices, photocatalytic degradation, electrochemical capacitors and other fields. For photocatalytic hydrogen production, POM such as $\text{XW}_{12}\text{O}_{40}^{n-}$ ($\text{X} = \text{Si, P, Fe, B or H}_2$) has been reported with photodeposition platinum as co-catalyst and methanol as sacrificial agent. The major challenge of photocatalytic hydrogen production is the recombination of charges and utilization of solar spectrum leads to efficiency loss. In order to promote the rapid surface transfer of photogenerated electrons and holes from photocatalyst, our previous studies used a fabrication process of photocatalytic films comprising Pt-NPs formed inside MCM-41 channels at the air-liquid interface. About utilization of solar spectrum, the widely used strategy for achieving this purpose is using sulphide, Nitrogen-doped or metal ion doped. In this work, we report an ions exchange synthesis for a UV-visible light-induced photocatalyst. Preparation of lacunary polyoxotungstate ($\text{PW}_{11}\text{O}_{39}^{7-}$; ℓ PTA) is by control pH and transition metal ion (Ni^{2+}) replaced WO^{4+} space, the UV-visible light-induced catalyst (Ni- ℓ PTA) be formed. The $[\text{XW}_{11}\text{O}_{39}]^{n-}$ monodeficient (lacunary) POM is formed by removing one single WO^{4+} unit from the complete Keggin structure, thereby resulting in a remarkable increase of the charge.

metal substitution at the vacant sites of lacunary POMs have been developed in efforts to utilize visible light. With IR and UV-vis spectrum, formations of ℓ PTA by control pH and the transition metal ion replace WO^{4+} space are traced. The structural evolution of the P-O stretching vibration mode reveals the ℓ PTA and transition metal ion replace for transition metal- ℓ PTA (Ni- ℓ PTA) formation. Using fabrication process of photocatalytic films comprising Pt-NPs formed inside MCM-41 channels at the air-liquid interface. Ni- ℓ PTA can be used as reducing agents to restore noble metal nanoparticles and can be coated on the surface of the nanoparticles to form a wrapping structure. The activity of this system can be expected to be improved further by high ordered allays of Pt NPs and M- ℓ PTA paired, which improve the separation and transportation of photo-induced electron-hole pairs and prevent the aggregation of co-catalyst NPs. As a result, the 6E-3M Ni- ℓ PTA exhibits prominent nearly 2 times higher photocatalytic hydrogen production rate of 35.5 $\mu\text{mol/hr}$, compared to the 3E-3M PTA.

Experiments

Preparation of ℓ PMS ($\text{Na}_7\text{PW}_{11}\text{O}_{39}$) and M- ℓ PTA:

$\text{Na}_7\text{PW}_{11}\text{O}_{39}$ was synthesized according to the literature. $\text{Na}_5\text{NiPW}_{11}\text{O}_{39}$ (Ni- ℓ PTA) was synthesized by modifying a method reported in the literature. The pre-synthesised intermediate, phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) was purchased from sigma-aldrich. A monovacant derivative, $\text{Na}_7\text{PW}_{11}\text{O}_{39}$, was synthesized from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ using methods described in literature by control pH~5 at 70 °C. $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ (1 g) was dissolved in 20 mL of water (pH 5) at 70 °C, followed by the dropwise addition of a 0.6 mM

Ni(NO₃)₂ (sigma-aldrich) aqueous solution (5 mL). The reaction continued under stirring at 70 °C for overnight. After filtering, the supernatant was subjected to slow evaporation giving yellow-green block (Ni-ℓPTA) powders.

Preparation of Ni-ℓPTA Template and Pt-NP@Ni-ℓPMS Film: ¹

Metal lacquary polyoxometalatesilica-surfactant films were self-assembled at the air-water interface from an acidic solution comprising: HCl, CTAB, TEOS and Ni-ℓPTA. The composition was used to form free-floating films of thermodynamically favoured silicatropic phase of 2D hexagonal (H) packing. The sample solution trough for film formation was sealed in an air-tight box at 318 K. Formation of a self-assembled Ni-ℓPMS template film free-floating at the air-water interface could be gradually thicken and matured within 120 minutes. Subsequently, a small amount of H₂PtCl₆ solution was injected into the solution under the Ni-ℓPMS template at air-water interface. Uniform adsorption of H₂PtCl₆ to the Ni-ℓPMS template was within 30 min. The H₂PtCl₆ adsorbed M-ℓPMS template at the air-water was then subjected to UV irradiation for a 30 min (with a xenon arc lamp) for the final product of Pt-NP@Ni-ℓPMS film.

Results & Discussion

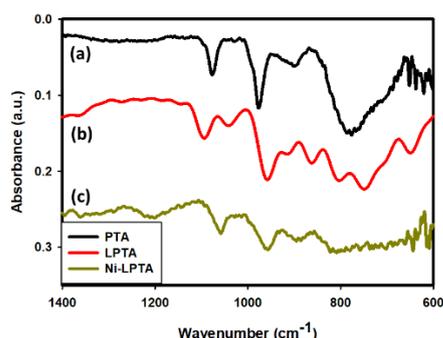


Fig. 1. IR spectra of PTA (a), ℓPTA (b) and Ni-ℓPTA (c).

Table 1. The assignment and wavenumber (cm⁻¹) of the vibration modes in the IR spectra of the complexes

	PTA	ℓPTA	Ni-ℓPTA
P-O _a stretching	1074	1090 1035	1061
W=O _d stretching	974	954	953
W-O _b -W stretching	892	905 863	888
W-O _c -W stretching	772	800 753	-

Figure 1 and Table 1 show the IR spectra of these POMs. They exhibit characteristic vibration patterns derived from the Keggin framework at 700–1100 cm⁻¹. The vibrational frequencies fall in the sequence of ν(P-O_a), ν(W=O_d), ν(W-O_b-W) and ν(W-O_c-M) for PTA, ℓPTA and Ni-ℓPTA. The spectrum of the PTA anion shows a prominent band at 1074 cm⁻¹ assigned to the ν(P-O_a) vibration of the central PO₄ tetrahedron. In the ℓPTA anion spectrum, this band is split into two components (1090 and 1035 cm⁻¹), due to the symmetry decrease of the PO₄ tetrahedron. For the Ni-ℓPTA anions, the value of the ν(P-O_a) PO₄ splitting

is always lower than that of the free ligand ℓPTA anion. The filling of the hole in the octahedral lacuna by the Ni²⁺ cation to some extent restores the symmetry of the central tetrahedron, owing to the interaction between Ni²⁺ and the available oxygen of the central PO₄ group (O_a). The ν values observed for the Ni-ℓPTA compounds (table 1) are in close agreement with those reported.

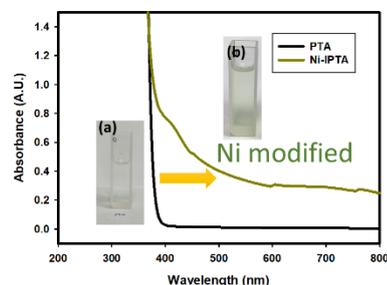


Fig. 2 UV-vis spectra of PTA (a) and Ni-ℓPTA (b).

Figure 2 shows absorption spectra of PTA (a) and Ni-ℓPTA. The absorption band is UV region which can be regarded as the charge-transfer of the bridge oxygen to metal atoms (O_b/O_c→W). The visible-light absorption that developed after the Ni modified was attributable to the MMCT of O_b/O_c→Ni.

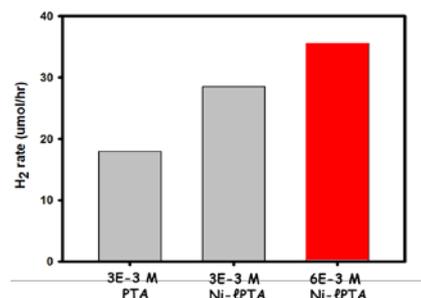


Fig. 3. Bar charts show the rate of hydrogen evolution for 3E-3M PTA, 3E-3M Ni-ℓPTA and 6E-3M Ni-ℓPTA with Pt-NPs@Ni-ℓPMS.

There are several conclusions can be drawn from the results of Fig 3. First, 6E-3M Ni-ℓPTA exhibits prominent nearly 2 times higher photocatalytic hydrogen production rate of 35.5 μmol/hr, compared to the 3E-3M PTA. It indicates that Ni-ℓPTA served as photocatalyst for the improvement of the absorption with UV and visible light. Secondly, 6E-3M Ni-ℓPTA exhibits prominent nearly 1.25 times higher photocatalytic hydrogen production rate, compared to the 3E-3M Ni-ℓPTA, indicating that Ni-ℓPTA is lower shadowing effect than PTA. In this work, the outcome indicates that Pt-NPs of ca. 2 nm with Ni-ℓPTA in silica channel improve the separation and transportation of photo-induced electron-hole pairs and prevent the aggregation of co-catalyst NPs. The Ni-ℓPTA can be proved extra absorption from UV extend to visible.

References

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