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Artificial photosynthesis for solar hydrogen generation over transition-metal substituted Keggin-type titanium tungstate

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Abstract

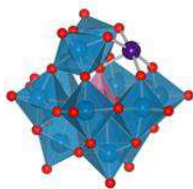
The photocatalytic hydrogen (H_2) evolution with transition-metal substituted Kegging-type titanium tungstate $Na_{5(6)}[MTiW_{11}O_{39}] \cdot xH_2O$ (abbreviated as $TiW_{11}M$ ($M=Fe,Co,Zn$)) as photocatalysts was reported. They showed good photocatalytic activities toward H_2 evolution in homogeneous systems under simulated solar light irradiation. The order of photocatalytic activity was $TiW_{11}Co \approx TiW_{11}Zn > TiW_{11}Fe \gg H_3PW_{12}O_{40}$ (PW_{12}). The selected POMs showed good stability during the reactions. Karl Fischer analysis, ICPE (Inductive Coupled Plasma Emission), FT-IR (Fourier Transform Infrared Spectroscopy) were used to confirm the composition and structure. UV-Vis absorption spectra, kinetics investigation, cyclic voltammetric characterizations were used to explain the photocatalytic result. At last, analogous “Z-scheme” mechanism was proposed for the homogeneous systems toward photocatalytic H_2 evolution under simulated solar light irradiation.

1. Introduction

In recent years, more and more attentions have been paid on conversion of solar energy into hydrogen energy as a clean and renewable energy carrier offering both high-energy capacity and minimal environmental impact by photocatalytic water splitting.¹⁻⁷ In this area, significant efforts have been made to exploit the metal oxide semiconductor (MOS) photocatalysts.⁸⁻¹¹ Polyoxometalates (POMs) are another large family of photoactive materials¹² that can work under both homogeneous and heterogeneous conditions. POMs are well-defined early transition metal-oxygen clusters, which have been drawn considerable interest because of their unique structural characteristics and their potential applications in photo-electro-catalysis.^{13,14} The photocatalytic H₂ evolution activity with various types of POMs,^{15,16-23} especially the Keggin-type heteropolytungstates (i.e., PW₁₂O₄₀³⁻, SiW₁₂O₄₀⁴⁻, FeW₁₂O₄₀⁵⁻, BW₁₂O₄₀⁵⁻, and H₂W₁₂O₄₀⁶⁻) structures have ever been reported. However, most of them are only active under UV irradiation. Thus it is very important to find out photocatalysts that can work under visible-light irradiation to meet the requirement of making full use of solar energy. Transition metal substituted polyoxometalates (TMSPs) have been reported that the electronic structure can be tuned through changing the transition metal ions participating in the substitution,²⁴ and meanwhile maintain high stability of most of their redox states and the possibility of multiple electron transfer,²⁵ thus it provides the chance to obtain materials with better visible light absorption ability. Recently, our group has reported the high nuclearity Co substituted polyoxometalates²⁶ that showed good photocatalytic activities toward H₂

evolution in both molecule scale (homogeneous) and composite (heterogeneous) systems under simulated solar light irradiation.

In an earlier report,²⁷ a series of transition metal substituted Keggin-structure undecatungstotitanates were synthesized. They were the first examples of inorganic room-temperature ionic liquids (ILs) consisting of an inorganic POM anion with the Keggin structure and a sodium ion, that is $\text{Na}_{5(6)}[\text{MTiW}_{11}\text{O}_{39}] \cdot x\text{H}_2\text{O}$ (abbreviated as TiW_{11}M) [where M=transition metal]. These compounds were miscible with water and showed good visible light absorption ability as the unique anion structure.²⁸ These characterizations may provide these compounds with good photocatalytic activities toward H_2 evolution under solar light irradiation. To the best of our knowledge, however, the photocatalytic H_2 evolution activity of these compounds had never been reported. Herein, we studied the photocatalytic activities of three compounds with different transition metal substitution that are TiW_{11}Co , TiW_{11}Zn and TiW_{11}Fe . The structure of the compounds was shown in Scheme 1. At the same time, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}), which was reported as the most efficient photocatalytic POM under UV-light irradiation, was taken as the contrast in homogeneous systems under simulated solar light irradiation. It was demonstrated that all of the three compounds showed good photocatalytic activity for H_2 evolution and the order was as follows: $\text{TiW}_{11}\text{Co} \approx \text{TiW}_{11}\text{Zn} > \text{TiW}_{11}\text{Fe} \gg \text{PW}_{12}$. At last, the mechanism of photocatalytic process was proposed as “Z-scheme”²⁹ that is simulated as occurred in plant photosynthetic systems.



Scheme 1 Polyhedral representation of the polyanions in the salts TiW_{11}M (M=Transition Metal). The central tetrahedron represents TiO_4 (pink), the polyhedras represent WO_6 (blue), M (purple) and O (red).

2. Experimental

2.1 Reagents and Materials

Polyvinyl alcohol (PVA) was purchased from Aldrich Chemical Company and was used as received. TiCl_4 , $\text{CH}_3\text{CH}_2\text{OH}$, HCl and CH_3COOH were purchased from Beijing Chemical Reagents Corporation. All other reagents were of analytical grade. Ultrapure water purified with Milli-Q (MQ) plus system (Millipore Co.) with resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was exclusively used in all aqueous solutions and rinsing procedures.

2.2 Catalyst preparation

$\text{Na}_5[\text{CoTiW}_{11}\text{O}_{39}] \cdot 28\text{H}_2\text{O}$ (**1**) was synthesized according to the report by Liyi Dai²⁷ with some modification. 36.3g (0.11 mol) of sodium tungstate was dissolved in 200 mL water. TiCl_4 (1.099 mL, 0.01 mol) was added to the solution with stirring violently. The mixture was filtered to remove the insolubles. The pH of filtrate was adjusted to 5.5-6 with glacial acetic acid. The mixture was refluxed at 333 K for half an hour, then about 5 mL of a solution containing 0.01 mol of cobalt chloride was added to the hot mixture. After stirring for 2.5 h at 333 K, the mixture was filtered and the filtrate was cooled to room temperature in a beaker. Anhydrous ethanol (50 mL)

was added to the cool filtrate. The product, a colored oil, was collected at the bottom of the beaker. Yield: ca. 30-35%. Karl Fischer analysis gave 28 water molecules of hydration. FT-IR (cm^{-1}): 932 (s), 874(s), 791(s), 698(w). Elemental analysis calculated (%) for $\text{Na}_5[\text{CoTiW}_{11}\text{O}_{39}] \cdot 28\text{H}_2\text{O}$: Na, 3.41; Co, 1.75; W, 60.00; Ti, 1.42. Found: Na, 3.38; Co, 1.76; W, 59.30; Ti, 1.38.

$\text{Na}_5[\text{FeTiW}_{11}\text{O}_{39}] \cdot 34\text{H}_2\text{O}$ (2) was synthesized by the same protocol as **1** but using FeCl_3 in the final reaction. Karl Fischer analysis gave 34 water molecules of hydration. FT-IR (cm^{-1}): 932 (s), 880 (s), 784 (s), 709 (w). Elemental analysis calculated (%) for $\text{Na}_5[\text{FeTiW}_{11}\text{O}_{39}] \cdot 34\text{H}_2\text{O}$: Na, 3.30; Fe, 1.61; W, 58.18; Ti, 1.37. Found: Na, 3.26; Fe, 1.65; W, 58.12; Ti, 1.35.

$\text{Na}_6[\text{ZnTiW}_{11}\text{O}_{39}] \cdot 28\text{H}_2\text{O}$ (3) was synthesized by the same protocol as **1** but using ZnCl_2 in the final reaction. Karl Fischer analysis gave 28 water molecules of hydration. FT-IR (cm^{-1}): 929 (s), 870 (s), 800 (s), 708 (w). Elemental analysis calculated (%) for $\text{Na}_5[\text{ZnTiW}_{11}\text{O}_{39}] \cdot 28\text{H}_2\text{O}$: Na, 4.0; Zn, 1.91; W, 59.48; Ti, 1.41. Found: Na, 3.86; Zn, 1.92; W, 59.12; Ti, 1.40.

2.3 Characterizations

Elemental analysis of the catalysts were determined by ICPE-9000, SHIMADZU. The water content was estimated by Karl Fischer analysis on ZDJ-ZS. The infrared spectra were recorded by Fourier Transform Infrared Spectroscopy (FT-IR) on a Spectrum GX spectrophotometer. Absorption spectras were recorded on a Varian Cary 5000 spectrophotometer. Cyclic Voltammetry (CV) experiments were carried out in a conventional three-electrode cell. A platinum foil (3.0 cm^2) and a saturated calomel

electrode (SCE) were used as counter and reference electrodes, respectively. The glassy carbon (GC) electrode was used as the working electrode. The electrolyte (0.05mM TiW_{11}M (M=Fe,Co,Zn) and 0.1M Na_2SO_4 in PVA aqueous 0.1 wt % solution, pH=1.0) was saturated with ultrahigh-purity Ar for 30 min before CV measurements.

2.4 Photocatalytic experiments

Photocatalytic experiments were conducted in a quartz flask (ca. 200 cm^3) sealed with a silicone rubber septum that has a top flat window ca. 38.5 cm^2 for irradiation. For the photocatalytic H_2 evolution, the photocatalysts of 0.05 mM TiW_{11}M (M=Fe,Co,Zn) or PW_{12} , were placed in 80 mL of 4 mg ml^{-1} PVA-water solution (pH=1.0) in the flask. PVA was employed as the electron donor. Before irradiation, Ar gas was purged into the solution for 40 min to remove the dissolved oxygen and ensure the reactor in an anaerobic condition. A homogeneous reactant mixture was maintained by means of a magnetic stirrer and the H_2 evolution was maintained at room temperature by providing a flow of cooling water during the photocatalytic reactions. The evolved H_2 was analyzed by a gas chromatograph (TCD, molecular sieve 5A column, Ar as the carrier). A simulated solar light lamp with the available spectral range from 350-760 nm (AM 1.5G) was used as the light source for the photocatalytic reactions.

2.5 Recycling experiments

Recycling experiments were carried out to study the stability of catalysts in solution. After 3 hours of the first time of photocatalytic experiment, silicone rubber septum

was taken out from the quartz flask (ca. 200 cm³) to make it open to the atmosphere. The color of solution in the quartz flask was totally colorless after standing for 24 hours, then the second time of photocatalytic experiment was conducted followed the same procedure described above in the photocatalytic experiments. Thus the experiments repeated further.

3. Results and Discussion

Fig. 1 shows the time courses of photocatalytic H₂ evolution over TiW₁₁M (M=Fe,Co,Zn) systems and PW₁₂ under simulated solar light (350-760 nm) irradiation. After 3 h of irradiation, the amounts of H₂ produced are 12.8, 12.4 and 7.5 μmol for TiW₁₁Co, TiW₁₁Zn and TiW₁₁Fe, respectively. Correspondingly, the turnover number (TON) [(moles of H₂ formed)/(moles of initial TiW₁₁M)] are 3.2, 3.1 and 1.88, respectively. However, scarcely any H₂ was produced in PW₁₂ system under the same irradiation condition. This showed that the three compounds exhibited better photocatalytic activity than PW₁₂ under present system and the activity order was as follows: TiW₁₁Co≈TiW₁₁Zn>TiW₁₁Fe>>PW₁₂.

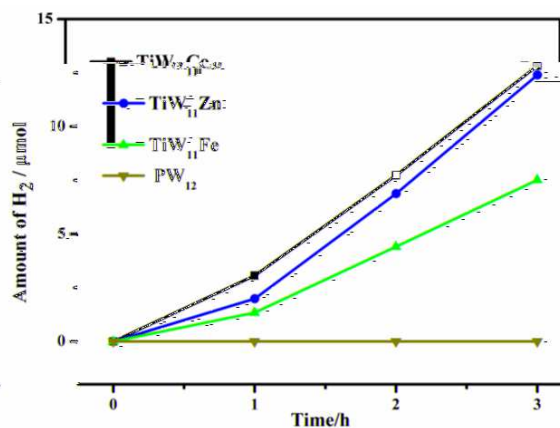


Fig. 1 Time courses of photocatalytic H₂ evolution over TiW₁₁M (M=Fe,Co,Zn) and PW₁₂ under simulated solar light (350-760 nm) irradiation. Reaction conditions: 0.05

mM TiW_{11}M or 0.05 mM PW_{12} , pH=1.0.

According to the principle of thermodynamic, photo-injection of electrons promotes the redox potential of the Keggin-type heteropolytungstates structures to more negative values sufficient to reduce H^+ under anaerobic condition. For Keggin-type heteropolytungstates structures, the pH value has significant influence on the redox potential which changes to positive potential with a slope of ~ 59 mV/pH with decreasing pH.²⁵ Thus, we took TiW_{11}Co as the representative compound to investigate the effect of pH value on photocatalytic ability for H_2 evolution. The results were showed in Fig. 2. It could be clearly observed that the photocatalytic activity of TiW_{11}Co was strongly dependent on the pH value of the solution and the optimal pH value was 1.0. With increase of the pH value, the photocatalytic activity decreased and disappeared after the pH value reach to 5. Further increase of pH value will not have key effect on the activity.

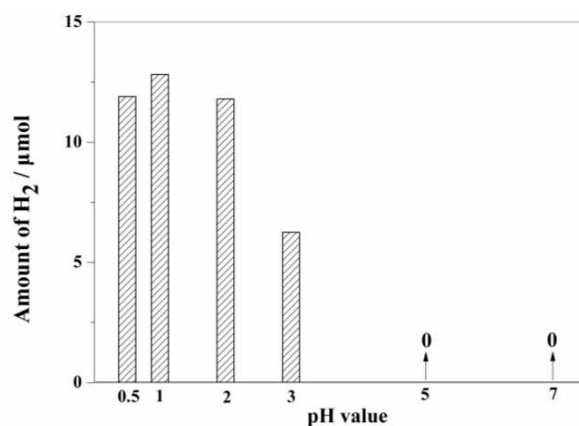


Fig. 2 Effect of pH value on photocatalytic activity for hydrogen evolution over TiW_{11}Co under simulated solar light (350-760 nm) irradiation. Reaction conditions: 0.05 mM TiW_{11}Co , irradiation time 3 h.

TMSPs are oxidatively and hydrolytically stable.³⁰ Recycling studies were performed in order to explore the stability of the catalysts. TiW_{11}Co was selected as the candidate for it showed the best photocatalytic H_2 evolution ability. As shown in Fig. 3, after three cycles of photocatalytic experiments, no obvious change of H_2 production was observed, which showed that the catalyst was stable.

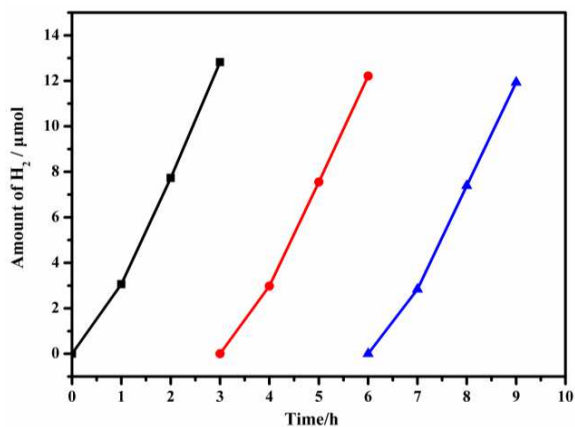


Fig. 3 Hydrogen production cycles (3 cycles) under simulated solar light (350-760 nm) irradiation. Reaction conditions: 0.05 mM TiW_{11}Co , pH=1.0.

For further clarify the difference in photocatalytic activities of the selected compounds, UV-visible spectra of the selected compounds were collected for comparison. Fig. 4 showed the UV-visible absorption spectra of TiW_{11}M (M=Fe,Co,Zn) and PW_{12} systems. It was obviously that TiW_{11}Co displayed two strong absorptions in the region at 350-700 nm. The strong absorption at 500-700nm is derived from the absorption of cobalt of d-d transition and the absorption at 400-500 nm belongs to O-Co charge transfer band.²⁸ TiW_{11}Zn showed contiguous absorption with TiW_{11}Co at 400-500 nm while TiW_{11}Fe just showed strong absorption in the near visible region. However, hardly any absorption could be seen of PW_{12} at 350-760nm according to the illustrated graph. The different absorption of the

compounds in the solar range may indicate the different photocatalytic activities.

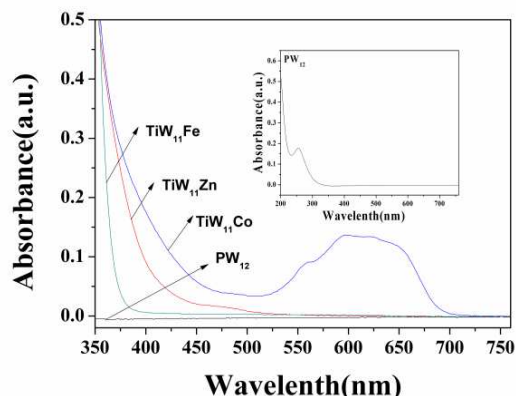


Fig. 4 UV-visible absorption spectras of TiW_{11}M ($\text{M}=\text{Fe},\text{Co},\text{Zn}$) and PW_{12} .

For further study the reason of different activities, electrochemistry of three ILs compounds was studied. It has come to light that the reduction potential of proton (E^0 , corresponding to the process $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) is dependent on the pH of the solution according to the Nernst equation $E^0 = -(0.242 + 0.059 \times \text{pH})$ V (vs. SCE). Under our reaction conditions, the E^0 was -0.301 V vs. SCE since the pH of the reaction mixture was 1.0. The results of CV experiments were shown in Fig. 5. It shows that all of three inorganic ILs compounds possess two pairs of reversible redox peaks between the potential range from -0.5V to 0V. The first pair of reversible peaks was assigned to the redox of Ti(III)/Ti(IV) in the TiW_{11}M ($\text{M}=\text{Fe},\text{Co},\text{Zn}$) anions.³¹ It was not energetically plausible to reduce H^+ to H_2 for the reduction potential was more positive than the E^0 in our experimental condition. The second pair is corresponding to the redox of W(V)/W(VI) in the title polyanions and it was demonstrated that the $E_{1/2}$ values for the second reduction waves are -0.44 V, -0.45 V and -0.46V vs. SCE for TiW_{11}Co , TiW_{11}Zn and TiW_{11}Fe , respectively, while that of PW_{12} are -0.266 V vs. SCE,¹⁶ which indicated that the reduced TiW_{11}M (HPB) ($\text{M}=\text{Fe},\text{Co},\text{Zn}$) are all

energetically plausible to reduce H^+ to H_2 while PW_{12} can hardly be reduced under the same conditions.

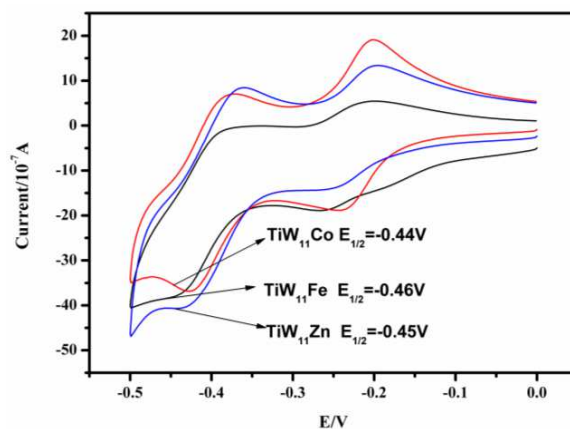


Fig. 5 Cyclic voltammograms of $TiW_{11}M$ ($M=Fe,Co,Zn$) at a scan rate of 10 mV s^{-1} . Conditions: $0.05\text{ mM } TiW_{11}M$, $0.1\text{ M } Na_2SO_4$ in PVA aqueous $0.1\text{ wt } \%$ solution was used as supporting electrolyte ($pH=1.0$).

For the sake of determining the exact mechanism of the homogeneous photocatalytic H_2 evolution of $TiW_{11}M$ ($M=Fe,Co,Zn$) systems under simulated solar light irradiation, different light sources ($350\text{-}400\text{ nm}$, $400\text{-}760\text{ nm}$ and $350\text{-}760\text{ nm}$) were used to investigate the H_2 evolution for $TiW_{11}Co$ (Fig. 6). It was illustrated that $TiW_{11}Co$ had only slight photocatalytic H_2 evolution activity under pure UV-light irradiation ($350\text{-}400\text{ nm}$) and there was no photocatalytic activity under pure visible light ($400\text{-}760\text{ nm}$) irradiation. Nevertheless, the activity for photocatalytic H_2 evolution was dramatically increased under full range simulated solar light ($350\text{-}760\text{ nm}$) irradiation.

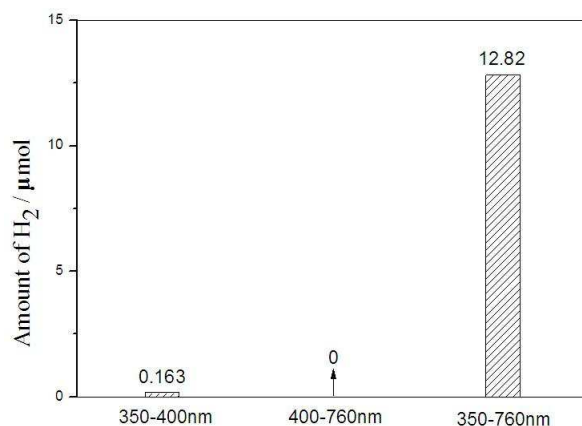
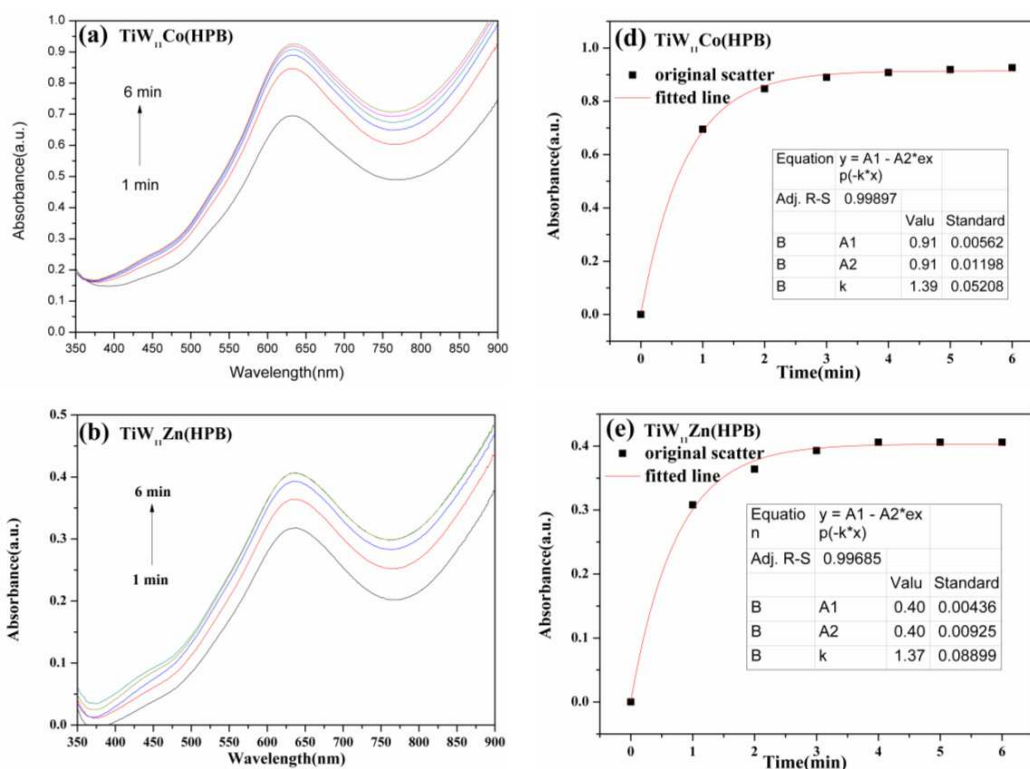


Fig. 6 H₂ evolution over TiW₁₁Co under the irradiation of different light sources (350-400 nm, 400-760 nm and 350-760 nm). Reaction conditions: 0.05 mM TiW₁₁Co, pH=1.0, irradiation time 3 h

It is well known that under UV-light irradiation, the POM could be excited and forms the POM^{*}, which can capture the electron from organic donor, thus yielding dark blue HPB.^{16,17} Formation of HPB occurs due to the trapping of d¹ electrons, which make HPB absorb visible light through d-d and/or intervalence charge-transfer band excitation.²² Then HPB can deliver electron to H⁺ and reduce it to H atom as shown in Scheme 2a. As was proved by CV, the HPB of the selected POMs are all energetically plausible to reduce H⁺ to H₂. However, because there is only a little UV light in simulated solar light, such process is very slow and only a little H₂ can be detected with same irradiation time. And with pure visible light irradiation, no HPB was obtained and thus no H₂ was detected. Thus it can be concluded that the concentration of obtained HPB plays a key role in photocatalytic activities of the POMs. The kinetics investigation of the HPB generation process was investigated by monitoring the absorbance changes at 634nm as a function of irradiation time of TiW₁₁M (M=Fe,Co,Zn) systems. As shown in Fig. 7, graphs a-c referred to the

absorbance spectras of the solution after irradiation with simulated solar light for different times (1-6 min) of TiW_{11}Co , TiW_{11}Zn and TiW_{11}Fe , respectively. It was obviously that all of them showed strong absorption at 634nm after irradiation, which was generally attributed to the d-d and intervalence charge transfer $\text{W(V)}/\text{W(VI)}$.³² Graphs d-f were separately standing for the kinetics fitted curves of the absorbance at 634nm as a function of irradiation time for TiW_{11}Co , TiW_{11}Zn and TiW_{11}Fe . It was shown that the absorbance variation over irradiation time were all fitted to be first order reaction, and the reaction rate constant (k) was calculated to be 1.39, 1.37 and 1.18, respectively, which showed good agreement with the activity order $\text{TiW}_{11}\text{Co} \approx \text{TiW}_{11}\text{Zn} > \text{TiW}_{11}\text{Fe}$.



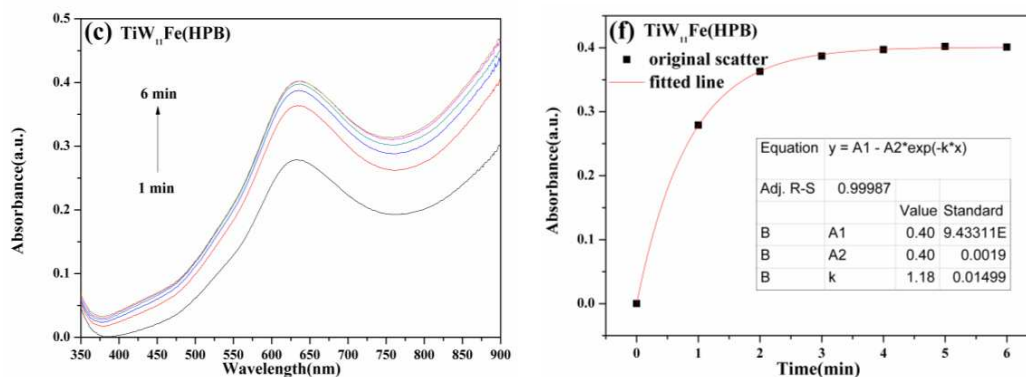
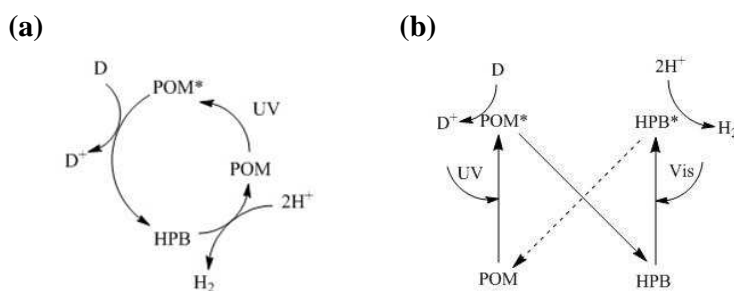


Fig. 7 Absorbance spectra of the solution after irradiation with simulated solar light for different times (1-6 min) (a-c) and kinetics fitted curves of the absorbance at 634nm as a function of irradiation time (d-f) for TiW_{11}Co , TiW_{11}Zn , and TiW_{11}Fe , respectively.

Given all this, a feasible photocatalytic H_2 evolution mechanism under simulated solar light was shown in scheme 2b, which was quite analogous to the “Z-scheme” encountered in plant photosynthetic systems.²⁹ The POM was firstly excited by UV-light (350-400 nm) and formed the POM^* , which captured the electron from organic donor (PVA), thus yielding dark blue HPB, then HPB absorbed visible light (400-760 nm) through d-d and/or intervalence charge-transfer band excitation and was re-excited to generate HPB^* . The reactivities of HPB^* was much higher than that of HPB, which led to higher H_2 evolution rate under simulated solar light irradiation. This process was further confirmed by the result (shown in ESI Fig. S1) of absorbance variation of HPB (TiW_{11}Co) over visible light (400-760 nm) irradiation time. After the simulated solar light (350-760 nm) irradiation for 6min, the solution turned to dark blue. Then the blue solution was exposed to visible light (400-760nm) irradiation, it was found that the blue color faded significantly and the absorbance of

HPB at 634 nm decreased and finally disappeared.



Scheme 2 Schematic diagrams of photocatalytic H_2 evolution of POMs under UV (a) or simulated solar light (b) irradiation. D means electron donor.

It should be noted that in our works, PVA was used as the electron donor/sacrificial. In fact, other simple alcohols such as methanol, 2-isopropanol were also used as sacrificial species (see ESI Fig. S2). PVA was found to display the highest activity. As PVA is rich in wastewater of textile and paper industries, this work may provide a new concept to use this considerable waste as useful agent.

4. Conclusions

In summary, artificial photosynthesis for solar hydrogen generation over transition-metal substituted Keggin-type titanium tungstate have been reported for the first time. It was demonstrated that the three compounds showed good photocatalytic activities toward H_2 evolution under simulated solar light irradiation and the order of photocatalytic activity was as follows: $\text{TiW}_{11}\text{Co} \approx \text{TiW}_{11}\text{Zn} > \text{TiW}_{11}\text{Fe} \gg \text{PW}_{12}$. The photocatalytic result was further confirmed by Cyclic Voltammetry (CV) characterization and kinetics investigation. Finally, analogous “Z-scheme”

mechanism has been proposed for the homogeneous systems under simulated solar light irradiation.

Acknowledgements

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