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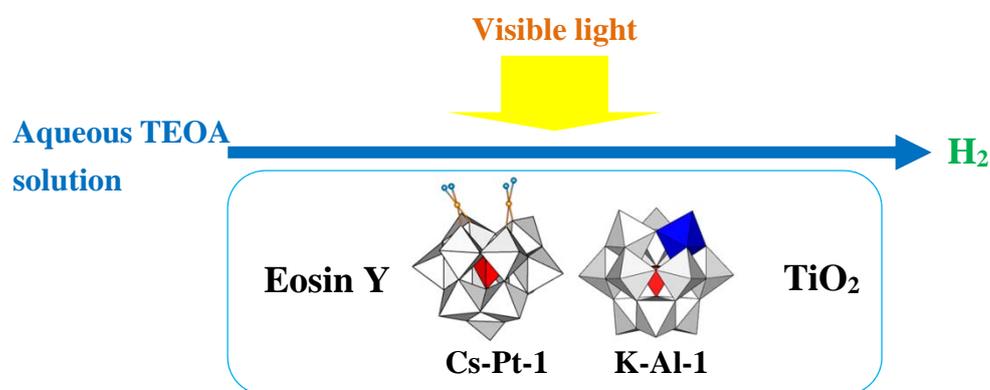
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Abstract: A novel photocatalytic system constructed using Eosin Y, α -Keggin-type diplatinum(II)-coordinated tungstophosphate $\text{Cs}_3[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}_2]\cdot 8\text{H}_2\text{O}$ (**Cs-Pt-1**), α -Keggin-type mono-aluminum(III)-coordinated tungstosilicate $\text{K}_5[\alpha\text{-SiW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]\cdot 7\text{H}_2\text{O}$ (**K-Al-1**), and titanium dioxide achieved a steady rate of hydrogen evolution with highly effective utilization of platinum sites from aqueous triethanolamine solution during a long-term visible light irradiation.

Graphical Abstract



Keywords Diplatinum(II) complex • Aluminum(III) complex • Polyoxometalate • Hydrogen evolution • Visible light

1. Introduction

Since Honda and Fujishima first demonstrated a photo-electrochemical cell, which consisted of a TiO₂ photo-anode and platinum cathode, that decomposed water into hydrogen and oxygen under ultraviolet (UV) irradiation with an external bias [1], the development of efficient photocatalysts, especially those that work under visible light irradiation, for the production of hydrogen from water has attracted attention of researchers working in the fields of solar light energy utilization and storage [2–4]. Platinum is known to be the most effective co-catalyst to construct efficient photocatalytic systems for producing hydrogen because platinum promotes the separation of photo-generated electrons and holes and improves the efficiency of photocatalysis when it acts as the active site for hydrogen evolution [5]. Therefore, further

improving the effective utilization of platinum sites is an important research objective.

To achieve an atomic-level utilization of platinum sites, we have earlier focused on the use of lacunary polyoxometalates as all-inorganic ligands because the coordination of metal ions and organometallic fragments into the vacant site(s) of lacunary polyoxometalates can be used to construct and stabilize well-defined metal centers [6–8]. Recently, we synthesized the cesium salt of α -Keggin diplatinum(II)-coordinated tungstophosphate, $\text{Cs}_3[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}_2]\cdot 8\text{H}_2\text{O}$ (**Cs-Pt-1**), and demonstrated its photocatalytic performance for hydrogen evolution from aqueous EDTA·2Na (ethylenediaminetetraacetic acid disodium salt) solution under visible light irradiation (≥ 400 nm) in the presence of titanium dioxide [9]. During the photoreactions, the platinum compound acted as both a photosensitizer and a co-catalyst, and exhibited high turnover numbers (TONs) when calculated on the basis of the amount of platinum atoms. The stability of the platinum centers was superior to cisplatin (*cis*-diamminedichloroplatinum(II)) under light irradiation. However, no reaction was observed under visible light irradiation at longer wavelengths because **Cs-Pt-1** only absorbs light at approximately 400 nm in the visible region.

Here, we demonstrated the photocatalytic performance of **Cs-Pt-1** in the presence of Eosin Y (EY) for hydrogen evolution from aqueous triethanolamine (TEOA) solutions under visible light irradiation ($\lambda = \geq 400$ nm and ≥ 440 nm). Although the rapid decomposition of EY under light irradiation caused a significant deactivation in the initial step, Li and co-workers recently reported that α -Keggin mono-aluminum-substituted tungstosilicate, $[\alpha\text{-SiW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]^{5-}$ (**Al-1**), stabilized EY via the coordination of EY onto the mono-aluminum site in polyoxoanion **Al-1** [10]. Thus, we also investigated the photocatalytic activities of the **Cs-Pt-1**/EY system in the presence of the Keggin- and Dawson-type mono- and multi-aluminum-coordinated polyoxometalates, $\text{K}_5[\alpha\text{-SiW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]\cdot 7\text{H}_2\text{O}$ (**K-Al-1**), $[(\text{CH}_3)_4\text{N}]_4[\alpha\text{-PW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]\cdot 8\text{H}_2\text{O}$ (**TMA-Al-2**), $\text{K}_6\text{Na}[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]\cdot 19\text{H}_2\text{O}$ (**KNa-Al-3**), $[(\text{CH}_3)_4\text{N}]_6\text{H}[\alpha_2\text{-P}_2\text{W}_{17}\{\text{Al}(\text{OH}_2)\}\text{O}_{61}]\cdot 11\text{H}_2\text{O}$ (**TMA-Al-4**), and $\text{K}_6[\text{B-}\alpha\text{-H}_3\text{P}_2\text{W}_{15}\{\text{Al}(\text{OH}_2)\}_3\text{O}_{59}]\cdot 14\text{H}_2\text{O}$ (**K-Al-5**). Finally, we constructed a novel photocatalytic system that achieved a steady rate of hydrogen production during a long-term light irradiation with highly effective utilization of the platinum sites over a wide visible region ($\lambda = \geq 400$ nm, ≥ 440 nm, and ≥ 500 nm). The molecular structures of **Cs-Pt-1**, **K-Al-1**, **TMA-Al-2**, **KNa-Al-3**, **TMA-Al-4**, and **K-Al-5** are shown in Figure 1.

(Insert Figure 1 here)

2. Experimental

2.1 Materials

Compounds **Cs-Pt-1**, **K-Al-1**, **TMA-Al-2**, **KNa-Al-3**, **K-Al-5**, and $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}]\cdot 17\text{H}_2\text{O}$ were synthesized using literature methods [9, 11–15]. Compound **TMA-Al-4** was synthesized analogously to the published method for $\text{K}_7[\alpha_2\text{-P}_2\text{W}_{17}\{\text{Al}(\text{OH}_2)\}\text{O}_{61}]\cdot 14\text{H}_2\text{O}$ [12]; the synthetic details and characterization results are shown in the Supporting Information. The number of solvated water molecules was determined using thermogravimetric/differential thermal analysis (TG/DTA). All of the reagents and solvents were obtained from commercial sources and used as received. Titanium dioxide (anatase:rutile = 80:20) was obtained from Wako Pure Chemical Industries, Ltd.

2.2 Instrumentation/Analytical Procedures

Elemental analysis was performed using a Mikroanalytisches Labor Pascher instrument (Remagen, Germany). The samples were dried overnight at ambient temperature under 10^{-3} – 10^{-4} Torr vacuum before analysis. The infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer on KBr disks at ambient temperature. TG/DTA data were obtained using Rigaku Thermo Plus 2 TG/DTA TG 8120 and Rigaku Thermo Plus EVO2 TG/DTA 81205Z instruments under air while increasing the temperature from 20 to 500 °C at a rate of 4 °C/min. The solution $^{31}\text{P}\text{-}\{^1\text{H}\}$ (242.95 MHz) nuclear magnetic resonance (NMR) spectra were recorded in 5-mm tubes on a JEOL ECA-600 NMR spectrometer. The ^{31}P NMR spectra were measured in D_2O with reference to an external standard of 85% H_3PO_4 in a sealed capillary. Chemical shifts were reported as negative on the δ scale for resonances upfield of H_3PO_4 (δ 0). Solution ultraviolet-visible (UV-Vis) spectra were recorded using a Perkin-Elmer Spectrum Lambda 650 spectrophotometer.

2.3 Photocatalytic Reaction Experiments

Typical photocatalytic reactions were carried out at 25 °C. **Cs-Pt-1** (0.2 – 1.0 μmol of Pt), EY (2.5 μmol), and aluminum-coordinated polyoxotungstates (2.5 μmol) were dissolved in 10 mL of 100 mM aqueous TEOA solution at pH 7.0. The solution was placed into a glass reaction vessel, which was connected to a Pyrex conventional closed gas circulation system (245.5 cm^3). The photoreaction was initiated by light irradiation using a 300 W Xe lamp equipped with a cut-off filter ($\lambda = \geq 400$ nm, ≥ 440 nm, or ≥ 500 nm). H_2 , O_2 , CO , and CH_4 evolution were analyzed using GC (TCD, Molecular Sieve 5A stainless columns). The samples were assigned after comparing them with standard samples analyzed under the same conditions. The turnover number (TON) was calculated as $2[\text{H}_2 \text{ evolved (mol)}]/[\text{Pt atoms (mol)}]$.

3. Results and Discussion

We examined the evolution of hydrogen from 100 mM aqueous TEOA solution (pH 7.0) under light irradiation (≥ 400 nm), as shown in Table 1. TEOA was used as an electron donor. During the photoreactions, the platinum and aluminum compounds and EY were soluble in the aqueous TEOA solution. Hydrogen was formed with 100% selectivity, and O_2 , CO_2 , CO , and CH_4 were not detected under these reaction conditions. When a mixture of **Cs-Pt-1** (0.2 μmol of Pt) and EY (2.5 μmol) was used as a catalyst, the initial reaction rates increased linearly; however, a rapid deactivation was observed after 4 h, as shown in Figure 2. The turnover frequency (TOF = TON h^{-1}) was 315 h^{-1} after 1 h, and the TON became 781 after 6 h. When cisplatin (1.0 μmol of Pt) was used, the TON was 88.6 after 6 h, which was lower than that of **Cs-Pt-1** (1.0 μmol of Pt; TON of 209 after 6 h) (Figure S1). Under ≥ 440 nm light irradiation, the **Cs-Pt-1** (1.9 μmol of Pt)/EY (5 μmol) system had a TOF of 70.4 h^{-1} (after 1 h) for hydrogen evolution from 100 mM aqueous TEOA solution (pH 10) (Figure S2), which was higher than that of a colloidal Pt (1.92 μmol)/EY (4.96 μmol) system for hydrogen evolution from 95 mM aqueous TEOA solution (pH 10) under >420 nm light irradiation (TOF of ~ 26.0 h^{-1} after 1 h) [10]. Here, we observed the stability of **Cs-Pt-1** during the photoreactions by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra in D_2O of a 100 mM aqueous TEOA solution containing **Cs-Pt-1** and EY after 1, 2, and 3-h light irradiation are shown in Figure S3. A signal was observed at -12.8 ppm, which was the same as that of as-prepared **Cs-Pt-1**, and no signal due to mono-lacunary α -Keggin polyoxotungstate was observed. These results suggested that the platinum sites in **Cs-Pt-1** were stable at least for a few hours under the present reaction conditions. Thus, the decrease in the reaction rates with time

would predominantly be caused by decomposition of EY.

To investigate the effect of aluminum-coordinated polyoxometalates for the photoreactions, aluminum compounds **K-Al-1**, **TMA-Al-2**, **KNa-Al-3**, **TMA-Al-4**, and **K-Al-5** were added to aqueous TEOA solutions containing **Cs-Pt-1** and EY, as shown in Table 1 and Figure 2. The initial reaction rates were markedly decreased in the presence of the aluminum compounds. The TOFs of **K-Al-1**, **TMA-Al-2**, **KNa-Al-3**, **TMA-Al-4**, and **K-Al-5** after 1 h were 170, 102, 116, 149, and 61.7 h⁻¹, respectively, which were lower than those in the absence of aluminum compounds (315 h⁻¹). This might have been caused by an anionic repulsion between the platinum- and aluminum-coordinated polyoxoanions. However, a clear deactivation was not observed after 12 h, and the **Cs-Pt-1/EY/K-Al-1** system showed a TON of 1042 after 12 h, which was higher than those in the presence of **TMA-Al-2** (652), **KNa-Al-3** (821), **TMA-Al-4** (853), and **K-Al-5** (965). When K₈[α-SiW₁₁O₃₉]·17H₂O (2.5 μmol) was added to the mixture of EY and **Cs-Pt-1** instead of the aluminum-coordinated polyoxometalates, the TON was 533 after 12 h. Therefore, the highest activities were obtained in the presence of **K-Al-1**, and both aluminum site and internal atom in **K-Al-1** affected the activities under these reaction conditions.

Under ≥440 nm light irradiation, the **Cs-Pt-1** (0.2 μmol of Pt)/EY (2.5 μmol)/**K-Al-1** (2.5 μmol) system produced 69.8 μmol of hydrogen after 12 h from a 100 mM aqueous TEOA solution at pH 7.0, and the TON became 698, as shown in Figure S4. No reaction was observed in the absence of EY under ≥440 nm light irradiation, which showed that the platinum sites in **Cs-Pt-1** worked as a co-catalyst. For the colloidal Pt (1.92 μmol)/EY (4.96 μmol) system, the initial rates increased with the addition of **K-Al-1** (96 μmol) [10]. However, the TON after 5 h was ~235 for hydrogen evolution from 95 mM aqueous TEOA solution (pH 7) under >420 nm light irradiation, which was lower than that of the **Cs-Pt-1/EY/K-Al-1** system (TON of 256 after 5 h) that was observed under ≥440 nm light irradiation.

The UV-Vis spectrum of a mixture of **Cs-Pt-1** (0.2 μmol of Pt), EY (2.5 μmol), and **K-Al-1** (2.5 μmol) in 100 mM aqueous TEOA solution at pH 7 is shown in Figure S5(a). All bands observed in the spectrum were the same as those of EY; thus, the bands due to **Cs-Pt-1** and **K-Al-1** were not observed because they were hidden by some large bands of EY. When the mixture was irradiated by light (≥400 nm), a large band at approximately 520 nm was sifted to approximately 490 nm, which was assigned to a fluorescein-like species [10,16] (Figure S5(b)). The shift was observed at least after 1-h light irradiation, and the absorbance of a band at 490 nm gradually decreased with time. Similar changes in UV-Vis spectra were observed in the presence

of **TMA-Al-2**, **KNa-Al-3**, **TMA-Al-4**, and **K-Al-5**. In the absence of aluminum-coordinated polyoxometalates, the all bands due to EY and fluorescein-like species completely disappeared after 6 h (Figure S5(c)). These results showed that aluminum-coordinated polyoxometalates remarkably stabilized EY and/or fluorescein-like species; however, it was reported that the activity of a fluorescein-like species was far lower than that of EY for hydrogen evolution from water [10]. Thus, a steady hydrogen production over a long-term of light irradiation would not be only caused by the stabilization of EY and/or fluorescein-like species. For the UV-vis measurements, a broad band at around 670 nm due to a heteropoly blue species was also observed for **Cs-Pt-1**/EY and EY/**K-Al-1**/cisplatin systems in a 100 mM aqueous TEOA solution at pH 7 after 1-h and 3-h light irradiation, as shown in Figure S6. As previously reported for Keggin-structure heteropoly blue anions/Pt/TiO₂ system [17], a heteropoly blue species can act as a photosensitizer for hydrogen evolution from water under light irradiation (>420 nm). In addition, a rapid deactivation observed for **Cs-Pt-1**/EY system was prevented at a higher platinum concentration, as shown in Figure S1. These results suggested that a heteropoly blue species derived from **Cs-Pt-1** and **K-Al-1** would compensate for the decline in hydrogen production.

When titanium dioxide (anatase:rutile = 80:20; 50 mg) was added to the **Cs-Pt-1** (0.2 μmol of Pt)/EY (2.5 μmol)/**K-Al-1** (2.5 μmol) system, the initial rates significantly increased under light irradiation (≥400 nm, ≥440 nm, and ≥500 nm), and a steady rate of hydrogen evolution was observed over 12 h (Figure 3). An induction period was observed under ≥440 nm and ≥500 nm light irradiation; however, it disappeared by using the **Cs-Pt-1**/EY/**K-Al-1**/TiO₂ system after 6-h light irradiation, as shown in Figure S7. The amounts of EY did not exert an effect to accelerate the initial rates. These results suggested that the process in a formation of heteropoly blue species affected the initial reaction rates. The amounts of hydrogen evolved after 12 h were 235.9, 160.7, and 24.1 μmol (with TONs of 2359, 1607, and 241), respectively. The TOFs after 1 h were 339 h⁻¹ (under ≥400 nm light irradiation) and 92.6 h⁻¹ (under ≥440 nm light irradiation). Although it is difficult to draw a simple comparison, the TOFs of various photocatalytic system containing dyes and platinum, e.g., bn(OH)₂-modified TiO₂ (0.1 wt% Pt) (bn(OH)₂ = 1,1'-binaphthalene-2,2'-diol) [18], Pt(dcbpy)(met)/platinized TiO₂ (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine; met = *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate) [19], EY sensitized mesoporous-assembled Pt/TiO₂ [20], Ru₂(bpy)₄L₁-PF₆, Pt/TiO₂ (bpy = 2,2'-bipyridine, L = μ-4,4'-azo-benzene carboxylic acid) [21], ruthenium(II)-bipyridyl dyes/Pt/TiO₂ [22], EY/SiW₁₁O₃₉⁸⁻/Pt/TiO₂ [23], Keggin-structure heteropoly blue anions/Pt/TiO₂ [17], EY/Pt/nitrogen-doped TiO₂ [24], coumarin or carbazole dyes/Pt/TiO₂ or H₄Nb₆O₁₇ [25], EY/Rose Bengal (RB)/Pt/graphene [26], RB/Pt/layered

double hydroxide [27], platinum nanoparticles inside the cavities of a fourth-generation polyamidoamine dendrimer decorated with $[\text{Ru}(\text{bpy})_3]^{2+}$ units [28], and cobalt(II)tetraphenylporphyrin/methylviologen/Pt-loaded poly (L-glutamate) [29], were lower than 90 h^{-1} for hydrogen evolution from aqueous solutions containing TEOA, diethanolamine, EDTA-2Na, methanol, glycerol, triiodide/iodide, or ascorbic acid under visible light irradiation ($\lambda = >400, >410, \geq 420, >430 \text{ nm}$, and $410 \text{ nm} < \lambda < 800 \text{ nm}$). In contrast, the TOFs of EY/Pt/modified TiO_2 with sulfate and phosphate [30], EY/ $\text{K}_7[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]/\text{Pt}$ [31], $[\text{RuL}(\text{bpy})_2](\text{PF}_6)_2/\text{Pt}/\text{TiO}_2$ (L = 2-hydroxyl-5-(imidazo-[4,5-f]-1,10-phenanthroline) benzoic acid [32], $\text{Ru}(\text{bpy})_2(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})^{2+}/\text{Pt}/\text{hexaniobate}$ nanoscrolls or acid-restacked calcium niobate nanosheets [33], and metal-free organic dyes containing benzo[*b*]phenothiazine/Pt/ TiO_2 [34] were in the range $100 - 840 \text{ h}^{-1}$ for hydrogen evolution from aqueous TEOA and EDTA solutions under visible light irradiation ($\lambda = >400$ and $\geq 420 \text{ nm}$); however, the rates rapidly decreased after a few hours. Therefore, the **Cs-Pt-1/EY/K-Al-1/TiO₂** photocatalytic system achieved high TOFs and steady hydrogen production over a long-term of light irradiation.

A probable energy diagram for the **Cs-Pt-1/EY/K-Al-1/TiO₂** system is shown in Figure S8. At the initial step, EY absorb photon energy to produce the excited EY*, and it injects electrons into the conduction band of TiO_2 and/or the tungsten sites in **Cs-Pt-1** and **K-Al-1** to form a heteropoly blue species. The electrons injected into the conduction band of TiO_2 are consumed by reduction of water at the platinum sites in **Cs-Pt-1** to form hydrogen. During the photoreactions, EY transformed into a fluorescein-like species. Both a fluorescein-like species and heteropoly blue species acted as a photosensitizer instead of EY in the later stage.

(Insert Table 1 and Figures 2 and 3 here)

4. Conclusion

We investigated a novel photocatalytic system constructed using EY, Keggin-type diplatinum(II)- and mono-aluminum(III)-coordinated polyoxometalates, and titanium dioxide for hydrogen production from aqueous TEOA solutions under visible light irradiation ($\lambda = \geq 400 \text{ nm}, \geq 440 \text{ nm}$, and $\geq 500 \text{ nm}$). The system achieved a steady hydrogen production during a long-term light irradiation with highly effective utilization of the platinum sites in a wide visible region.

Acknowledgments

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Figure captions

Figure 1. Polyhedral representations of polyoxoanions (a) $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}_2]^{3-}$ (**Pt-1**), (b) $[\alpha\text{-SiW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]^{5-}$ (**Al-1**) and $[\alpha\text{-PW}_{11}\{\text{Al}(\text{OH}_2)\}\text{O}_{39}]^{4-}$ (**Al-2**), (c) $[(\text{A-PW}_9\text{O}_{34})_2\{\text{W}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\text{OH})(\text{OH}_2)\}\{\text{Al}(\mu\text{-OH})(\text{OH}_2)_2\}_2]^{7-}$ (**Al-3**), (d) $[\alpha_2\text{-P}_2\text{W}_{17}\{\text{Al}(\text{OH}_2)\}\text{O}_{61}]^{7-}$ (**Al-4**), and (e) $[\text{B-}\alpha\text{-H}_3\text{P}_2\text{W}_{15}\{\text{Al}(\text{OH}_2)\}_3\text{O}_{59}]^{6-}$ (**Al-5**). The WO_6 and AlO_6 units are represented by white and blue octahedra, respectively. The internal PO_4 and SiO_4 units are represented by red tetrahedra. **Al-1**, **Al-2**, and **Al-4** were monomeric compounds where an aluminum ion was located at the A-site of the α -Keggin structure and at the B-site of the α -Dawson structure, respectively. Polyoxoanion **Al-3** was a dimeric aluminum complex where two 6-coordinate aluminum ions are linked by two bridging hydroxyl groups and four water molecules, i.e., $[\text{Al}^{\text{III}}_2(\mu\text{-OH})_2(\text{OH}_2)_4]^{4+}$. Units of a 6-coordinate tungsten and aluminum ions linked with a hydroxyl group and a water molecule, i.e., $[\text{W}(\text{OH})(\text{OH}_2)]^{5+}$ and $[\text{Al}(\text{OH})(\text{OH}_2)]^{2+}$ were sandwiched between two tri-lacunary α -Keggin polyoxotungstates. Polyoxoanion **Al-5** was also a monomeric compound where three aluminum ions were located at the B-site of the α -Dawson structure.

Figure 2. Time course for hydrogen evolution from aqueous TEOA solution under visible light irradiation catalyzed by **Cs-Pt-1** and EY without aluminum-coordinated polyoxometalates (\diamond), and in the presence of **K-Al-1** (\bullet), **TMA-Al-2** (\blacksquare), **KNa-Al-3** (\blacklozenge), **TMA-Al-4** (\circ), and **K-Al-5** (\square). Reaction conditions are shown in Table 1.

Figure 3. Time course for hydrogen evolution from aqueous TEOA solution under visible light irradiation. Reaction conditions: **Cs-Pt-1** (0.2 μmol of Pt), EY (2.5 μmol), **K-Al-1** (2.5 μmol), TiO_2 (anatase: rutile = 80 : 20) 50 mg, 100 mM TEOA aqueous solution (10 mL, pH 7), light irradiation at ((a) ≥ 400 nm, (b) ≥ 440 nm, and (c) ≥ 500 nm) at 25 $^\circ\text{C}$.

Table 1 Hydrogen evolution from TEOA aqueous solution catalyzed by platinum complexes and Eosin Y under visible light irradiation^a

Pt complexes (μmol of Pt atom)	Al-POMs	Reaction time (h)	H ₂ (μmol)	TON ^b
Cs-Pt-1 (0.2)	–	1	31.5	315
		6	78.1	781
Cs-Pt-1 (1.0)	–	1	35.4	70.7
		6	104.4	210
cisplatin (1.0)	–	1	34.2	68.4
		6	44.3	88.6
Cs-Pt-1 (0.2)	K-Al-1	1	17.0	170
		6	71.5	715
		12	104.2	1042
Cs-Pt-1 (0.2)	TMA-Al-2	1	10.2	102
		6	38.5	385
		12	65.2	652
Cs-Pt-1 (0.2)	KNa-Al-3	1	11.6	116
		6	63.6	636
		12	82.1	821
Cs-Pt-1 (0.2)	TMA-Al-4	1	14.9	149
		6	64.4	644
		12	85.3	853
Cs-Pt-1 (0.2)	K-Al-5	1	6.17	61.7
		6	61.2	612
		12	96.5	965
–	K-Al-1	1	trace	–
		6	trace	–

^aReaction conditions: platinum complexes (0.2 – 1.0 μmol of Pt), Al-POMs (2.5 μmol), EY (2.5 μmol), 100 mM TEOA aq. soln. (pH 7; 10 mL), 25 °C, light (≥ 400 nm)

^bTurnover number (TON) = 2[H₂ evolved (mol)]/[Pt atoms (mol)]

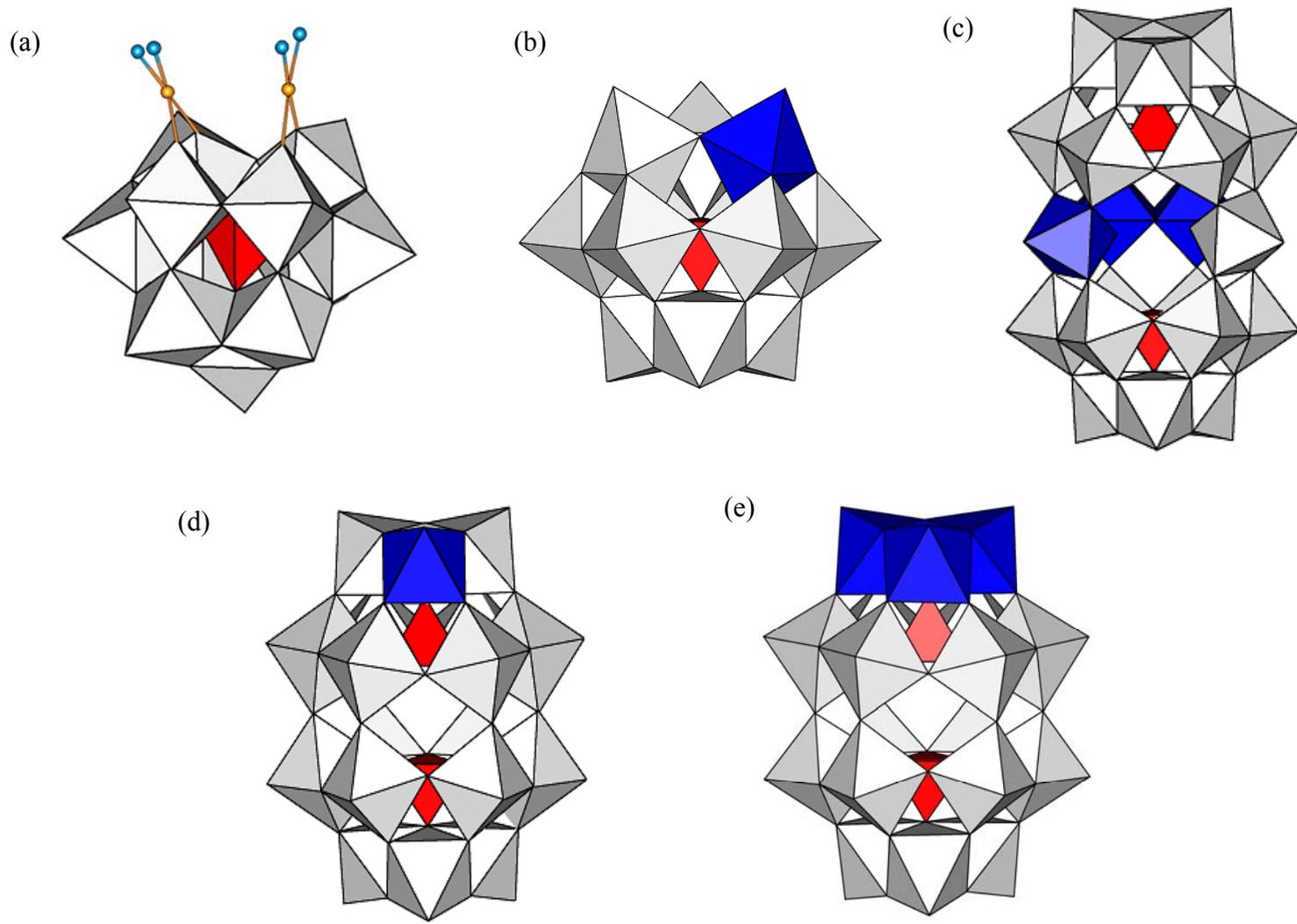


Fig. 1

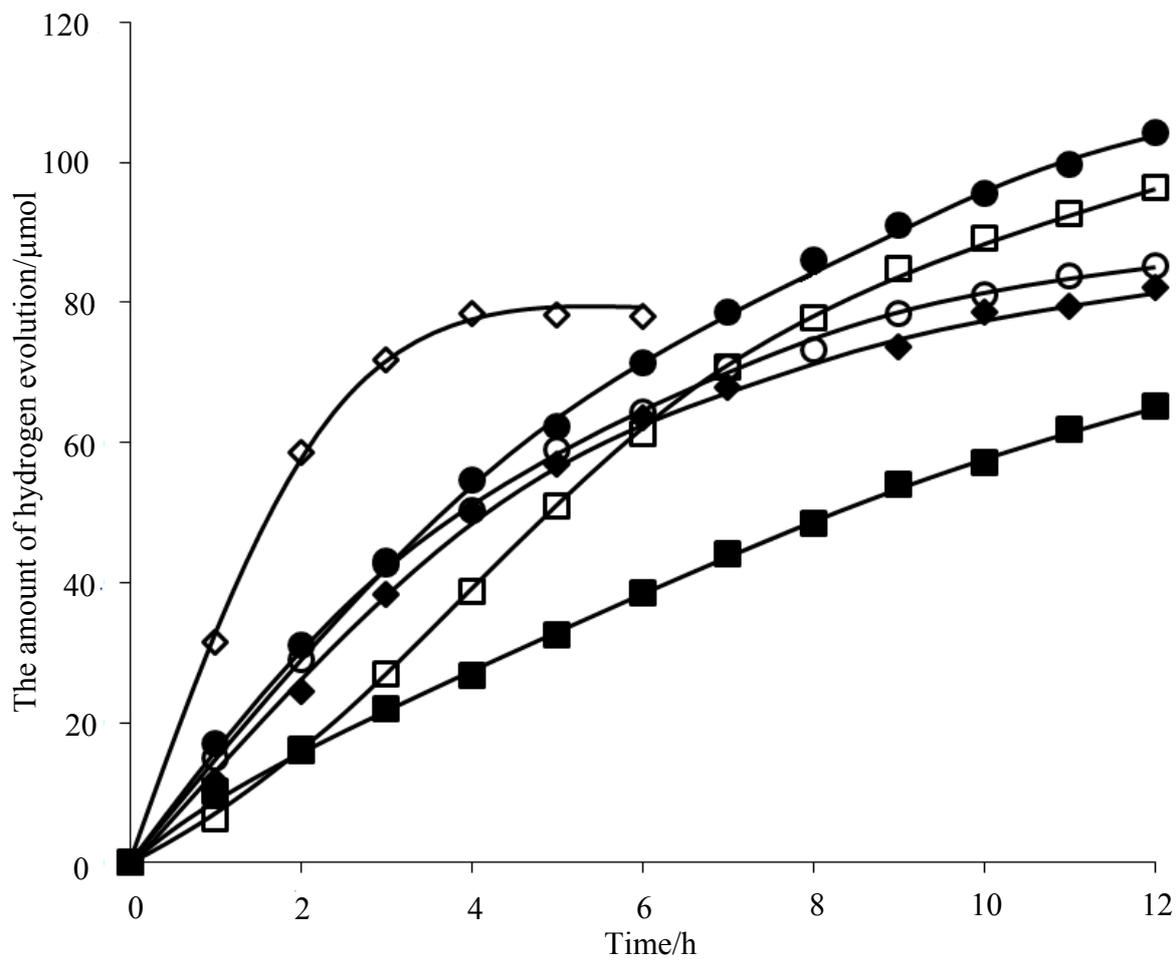


Fig. 2

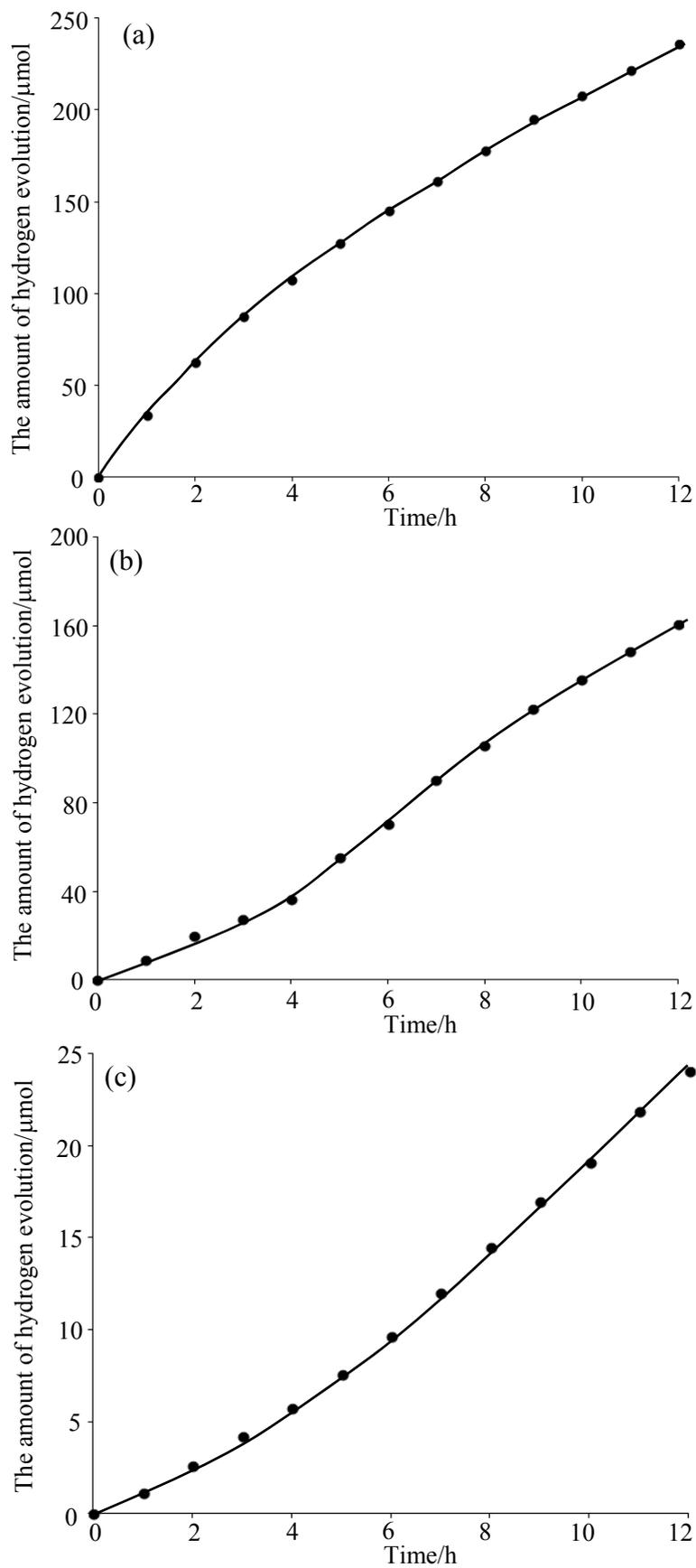


Fig. 3