



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



An effective preparation method of composite photocatalysts for hydrogen evolution using an organic photosensitizer and metal particles assembled on alumina-silica

Yusuke Yamada^{a,*}, Hideyuki Tadokoro^b, Shunichi Fukuzumi^{c,d,**}

^a Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

^b Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

^c Faculty of Science and Engineering, Meijo University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-0073, Japan

^d Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Republic of Korea

ARTICLE INFO

Article history:

Received 25 October 2015

Received in revised form

24 December 2015

Accepted 5 January 2016

Available online xxx

Keywords:

Photocatalyst

Hydrogen production

Preparation method

Organic photosensitizer

ABSTRACT

Composite catalysts for photocatalytic hydrogen (H_2) evolution were prepared by loading an organic electron donor-acceptor linked dyad [2-phenyl-4-(1-naphthyl)quinolinium ion, $QuPh^+-NA$] as an organic photosensitizer and Pt or Cu particles as H_2 -evolution catalysts on alumina-silica. The composite catalysts loading Pt particles were prepared by two different methods; first, Pt particles were deposited by reduction of $PtCl_6^{2-}$ owing to photocatalysis of $QuPh^+-NA$ supported on alumina-silica (PD method), and second, alumina-silica was impregnated with the $PtCl_6^{2-}$ and calcined, and then $QuPh^+-NA$ was loaded on the Pt/alumina-silica by a cation exchange method (IMP method). When a composite catalyst was prepared by the IMP method, a high Pt-loading amount of 4.2 wt% was necessary to achieve the highest H_2 -evolution rate of $0.27 \mu\text{mol h}^{-1}$. On the other hand, a composite catalyst prepared by the PD method exhibited three times faster H_2 evolution ($0.83 \mu\text{mol h}^{-1}$) even though the loading amount of Pt was as low as 0.4 wt%. The activity of composite catalysts prepared by the PD method highly depends on the electric charges of precursors for Pt particles. A composite catalyst prepared with positively charged $Pt(NH_3)_4^{2+}$ as a precursor of Pt particles exhibited low catalytic activity with the H_2 -evolution rate of $0.10 \mu\text{mol h}^{-1}$, which is significantly lower than the rate ($0.27 \mu\text{mol h}^{-1}$) for the composite catalyst prepared with $PtCl_6^{2-}$. However, such precursor-dependence was not observed for composite catalysts employing Cu particles as an H_2 -evolution catalyst, because the Cu precursors are more labile than the Pt precursors in a reaction solution. The electrostatic interaction between the precursors of metal particles and negatively charged surfaces of alumina-silica should be taken into account to construct efficient H_2 -evolution catalysts.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Utilization of solar energy to produce high-energy compounds such as hydrogen (H_2) attracts much attention to realize environmentally benign and sustainable society [1–5]. Two typical photocatalytic H_2 -evolution systems have been extensively studied. One is a system using a semiconductor photocatalyst, which

can split water to H_2 and O_2 under UV irradiation [6–9]. The fine-tuning of the bandgap of a metal oxide semiconductor photocatalyst by doping nitrogen or sulfur has enabled to utilize visible light for the photocatalytic H_2 production from water [10,11]. However, the quantum efficiency under visible light has remained low for any practical applications. The other system for photocatalytic H_2 production utilizes metal complexes or organic molecules as photosensitizers together with a water reduction catalyst in homogeneous systems for efficient utilization of visible light [12–23]. In these systems sacrificial electron donors are required for the H_2 evolution. To replace sacrificial electron donors to water as an electron donor, combination of the H_2 -evolution systems with water oxidation catalysts is necessary [24–33]. However, simple combination of water oxidation catalysts with water reduction

* Corresponding author.

** Corresponding author at: Faculty of Science and Engineering, Meijo University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-0073, Japan.

E-mail addresses: ymd@chem.eng.osaka-cu.ac.jp (Y. Yamada), fukuzumi@chem.eng.osaka-u.ac.jp (S. Fukuzumi).

<http://dx.doi.org/10.1016/j.cattod.2016.01.018>

0920-5861/© 2016 Elsevier B.V. All rights reserved.

catalysts in a solution results in the reversed flow of electrons from the reduced water reduction catalysts to the oxidized water oxidation catalysts. The undesired back electron transfer can be avoided by rational arrangement of photosensitizers and catalysts for water oxidation and reduction on a suitable support, where the movement of each component can be suppressed. Development of procedure to prepare composite catalysts having rational arrangement of each component on the support is crucial to construct H₂-evolution systems utilizing visible light.

Before constructing a fully assembled catalyst, we have combined an organic photosensitizer [2-phenyl-4-(1-naphthyl)quinolinium ion, QuPh⁺-NA] and a water reduction catalyst (Pt, Cu, etc.) on alumina-silica, which successfully exhibited photocatalytic activity for the H₂ evolution employing oxalate as an electron donor [34]. QuPh⁺-NA is an electron donor-acceptor linked dyad which possesses not only an extremely long lifetime of an electron-transfer state but also strong oxidizing and reducing abilities under photoirradiation [35]. The chemical structure of QuPh⁺-NA used in this study and the overall photocatalytic cycle for H₂ evolution are depicted in Scheme 1 [36–42]. The catalytic cycle starts from photoexcitation of QuPh⁺-NA in which electron transfer from the NA moiety to the singlet excited state of the QuPh⁺ moiety occurs to produce the electron-transfer state (QuPh^{•+}-NA^{•+}). Then, electron transfer from oxalate to QuPh^{•+}-NA^{•+} occurs to produce CO₂ and CO₂^{•-} and QuPh^{•+}-NA. CO₂^{•-} can transfer an electron to QuPh^{•+}-NA to produce CO₂ and QuPh^{•+}-NA. Two equivalents of QuPh^{•+}-NA thus produced can inject two electrons to metal nanoparticles to produce H₂ by reduction of two protons. In our previous work, combined catalysts were successfully prepared by the following two-step route (**PD** method): QuPh⁺-NA was first loaded on alumina-silica (QuPh⁺-NA@Al₂O₃-SiO₂) by the cation exchange method and then, Pt or Cu particles were supported on the QuPh⁺-NA@Al₂O₃-SiO₂ by the reduction of PtCl₆²⁻ or CuCl₂ *in situ* with photogenerated QuPh^{•+}-NA [34]. However, preparation conditions to achieve highly active composite catalysts have yet to be clarified in terms of choices of precursors, and nanostructures and morphologies of alumina-silica supports, etc.

We report herein the effect of preparation conditions of the catalysts composed of alumina-silica loading QuPh⁺-NA and Pt particles on their catalysis for photocatalytic H₂ evolution using oxalate as a sacrificial electron donor. Other than the **PD** method, the impregnation method (**IMP** method), in which alumina-silica was impregnated with Pt and then loading QuPh⁺-NA by the cation-exchange method, was examined to construct a composite catalyst. Also, various types of Pt complexes and Pt salts were examined as precursors of Pt particles for the **PD** method. Additionally, nanostructures and morphologies of alumina-silica supports were optimized for further improvement in the photocatalytic reactivity. Suitable preparation conditions were also investigated for a composite catalyst employing Cu particles, which has been less studied as an H₂-evolution catalyst.

2. Experimental

2.1. Catalyst preparation

All chemicals were obtained from chemical companies and used without further purification. K₂Pt^{IV}Cl₆, Pt^{II}(NH₃)₄Cl₂, K₂Cu^{II}Cl₄·2H₂O, Ru^{III}Cl₃, Co^{II}(NO₃)₂, Fe^{II}SO₄·7H₂O, cetyltrimethylammonium bromide (CTAB), sodium aluminate, acetic acid, hydrochloric acid and sodium hydroxide were obtained from Wako Pure Chemical Industries. K₂Pt^{II}Cl₄ was purchased from Sigma-Aldrich. An aqueous solution of ammonia (28%) and β-nicotinamide adenine dinucleotide disodium salt (reduced form) (NADH) were obtained from Tokyo Chemical Industry. Tetraethyl

orthosilicate (TEOS) was delivered by Shin-Etsu Chemical. 2-Phenyl-4-(1-naphthyl)quinolinium (QuPh⁺-NA) perchlorate was synthesized by a literature method [35]. Purified water was provided by a Millipore MilliQ UV-3 water purification system where the electronic conductance was 18.2 MΩ cm. Spherical Al-MCM-41 (sAlMCM-41), spherical Al₂O₃-SiO₂ (sAl₂O₃-SiO₂) and unshape-controlled Al₂O₃-SiO₂ (Al₂O₃-SiO₂) were prepared by literature methods [39]. *cis*-[Pt₂(NH₃)₂(μ-C₂H₄NO)₂](ClO₄)₂, [Cu(bpy)₂](NO₃)₂·0.75H₂O and [Cu(MeObpy)₂](NO₃)₂ were also synthesized by literature methods [43].

Unshape-controlled AlMCM-41 (uAlMCM-41) was prepared by the following procedure. To an aqueous solution (1.0 L) containing NaOH (8.4 g, 0.21 mol) and CTAB (18.4 g, 44.4 mmol) was added dropwise of TEOS (87.5 g, 418 mmol) with vigorous stirring for 1 h at 35 °C. The solution was further stirred for 30 min at the temperature. Then, an aqueous solution (100 mL) of sodium aluminate (0.48 g, 7.9 mmol) was slowly added to the solution and stirred for 4 h at room temperature. The obtained white precipitate was filtered, washed with water and dried at 60 °C. The precipitate was calcined at 500 °C for 6 h with a ramp rate of 1 °C min⁻¹.

Unshape-controlled Al₂O₃-SiO₂ was prepared by the surface alumination of unshaped silica powder. Silica powder (10–20 nm, 3.0 g, 50 mmol) was suspended in an aqueous solution (150 mL) of sodium aluminate (0.19 g, 3.1 mmol) with magnetic stirring at room temperature for 24 h. The obtained powder was collected by centrifugation, washed with water, and dried at 60 °C. The obtained white powder was calcined at 550 °C for 5 h with a ramp rate of 1 °C min⁻¹.

sAlMCM-41 loading Pt (Pt/sAlMCM-41) was prepared by an impregnation method. sAlMCM-41 (500 mg) was immersed in an ethanol solution (1.0 mL) containing a calculated amount of K₂PtCl₆ on an ultrasonicator for 30 min at room temperature. The powder was dried at 60 °C in air and calcined at 500 °C for 4 h with a ramp rate of 2 °C min⁻¹. The loading amount of Pt was determined by X-ray fluorescence measurements performed with a Rigaku ZSX-100e.

Alumina-silica loading QuPh⁺-NA was prepared by the cation-exchange method. An acetonitrile solution (10 mL) of QuPh⁺-NA (6.0 mM or 2.0 mM) was slowly added to an aqueous suspension (10 mL) containing alumina-silica (200 mg) with gentle magnetic stirring. After keeping for a certain time at room temperature, the supernatant was removed and dried at 60 °C. The amount of QuPh⁺-NA was determined by the decrease of absorbance at 333 nm originated from QuPh⁺-NA ion. The same procedure was applied for loading QuPh⁺-NA on Pt/sAlMCM-41 to achieve a composite catalyst (**IMP** method). Composite catalysts prepared by the **PD** method were obtained by photoirradiation (λ > 340 nm) of suspension containing alumina-silica loading QuPh⁺-NA, K₂PtCl₆ and oxalic acid. The obtained catalysts were used for the catalysis measurements without isolation.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) was used for the determination of the sizes and shapes of catalysts. Bright field images were obtained by a JEOL JEM-2100 that has a thermal field emission gun with an accelerating voltage of 200 kV. The observed samples were prepared by dropping a suspension of catalysts, allowing the solvent to evaporate and then scooped up with an amorphous carbon supporting film. Nitrogen adsorption-desorption at 77 K was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass of ~100 mg was used for adsorption analysis after pretreatment at 120 °C for 1 h under vacuum conditions and kept in N₂ atmosphere until N₂-adsorption measurements. The samples were exposed to a mixed gas of He and N₂ with a programmed ratio and adsorbed

Download English Version:

<https://daneshyari.com/en/article/4757246>

Download Persian Version:

<https://daneshyari.com/article/4757246>

[Daneshyari.com](https://daneshyari.com)