

Electronic Supplementary Information

for

Hybrid H₂-evolution catalysts: in-situ formation of H₂-evolution catalysts from metal salts inside the mesopores of silica-alumina supporting an organic photosensitiser

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

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

^b Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea

* To whom correspondence should be addressed.

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

Experimental Method

Materials. All chemicals were obtained from chemical companies and used without further purification. $K_2Pt(IV)Cl_6$ was purchased from Sigma–Aldrich. Sodium aluminate, acetic acid, hydrochloric acid and sodium hydroxide were obtained from Wako Pure Chemical Industries. Cetyltrimethylammonium bromide and sodium borohydride were purchased from Kanto Chemical. An aqueous solution of ammonia (28%) and β -nicotinamide adenine dinucleotide disodium salt (reduced form) (NADH) were obtained from Tokyo Chemical Industry. Tetraethyl orthosilicate was delivered by Shin-Etsu Chemical. An aqueous solution of colloidal Pt nanoparticles (~2 nm, 4 wt%) capped with polyvinylpyrrolidone was purchased from Tanaka Kikinzoku Kogyo K. K. 2-Phenyl-4-(1-naphthyl)quinolinium perchlorate ($QuPh^+-NA$) was synthesized by reported methods.^{S1} Purified water was provided by a Millipore MilliQ water purification system where the electronic conductance was 18.2 M Ω cm.

Synthesis of sAIMCM-41.^{S2} sAIMCM-41 with spherical shape was prepared by following a reported procedure. Cetyl trimethylammonium (14.6 g, 40.1 mmol) was dissolved to a mixed solvent of water (270 g) and ethanol (350 g) at room temperature. An aqueous ammonia solution (25%, 100 g) was added to the solution with vigorous stirring for 15 min and then tetraethyl orthosilicate (27.4 g, 131 mmol) for 2 h. The obtained slurry was placed at room temperature for 20 h and the formed precipitate was collected by filtration. The obtained precipitate was washed with an ethanol solution (100 g) containing ammonium nitrate (500 mg, 6.25 mmol) at 60 °C, then, water and ethanol, successively. The precipitate was collected by filtration and dried at 200 °C. The obtained spherical MCM-41 was suspended to an aqueous solution (400 mL) of sodium aluminate (0.510 g, 8.31 mmol) and stirred for 20 h at room temperature. The precipitate was collected by filtration and dried at 200 °C for 1 h. The dried sample was calcined at 550 °C for 6 h under atmospheric conditions to obtain sAIMCM-41.

Transmission Electron Microscopy (TEM) and X-ray fluorescence measurements.

The sizes and shapes of sAIMCM-41 was determined from bright field images using a JEOL JEM-2100 that has a cold field emission gun with an accelerating voltage of 200 keV. The observed samples were prepared by dropping a dispersion of catalysts and allowing the solvent to evaporate and then scooped up with an amorphous carbon supporting film. X-ray fluorescence measurements were performed with a Rigaku ZSX-100e to determine the concentration of catalysts compositions.

N₂ Adsorption for BET Surface Area Determination. 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 amount of N₂ was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min). The surface area of each catalyst was determined by the Brunauer-Emmett-Teller (BET) method for multiple N₂ adsorption amounts under the conditions of partial pressure less than 0.3.

Photocatalytic H₂ Evolution. An aqueous suspension (phthalate buffer, pH 4.5, 2.0 mL) containing QuPh⁺-NA@sAIMCM-41 composite (QuPh⁺-NA: 0.22 mM), NADH (1.0 mM) and an H₂-evolution catalyst was flushed with N₂ gas. The suspension was then photoirradiated for a certain time with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a colour filter glass (Asahi Techno Glass L39) transmitting $\lambda > 340$ nm at room temperature. After 1 min stirring in the dark, gas in a headspace was analysed by Shimadzu GC-14B gas chromatography (detector: TCD, column temperature: 50 °C, column: active carbon with the particle size 60-80 mesh, carrier gas: N₂ gas) to determine the amount of evolved H₂.

References

- S1. H. Kotani, K. Ohkubo and S. Fukuzumi, *Faraday Discuss.*, 2012, **155**, 89.
- S2. (a) Á. Szegedi, Z. Kónya, D. Méhn, E. Solymár, G. Pál-Borbély, Z. E. Horváth, L. P. Biró and I. Kiricsi, *Appl. Catal., A*, 2004, **272**, 257; (b) O. A. Anunziata, M. L. Martínez and M. G. Costa, *Mater. Lett.*, 2010, **64**, 545.

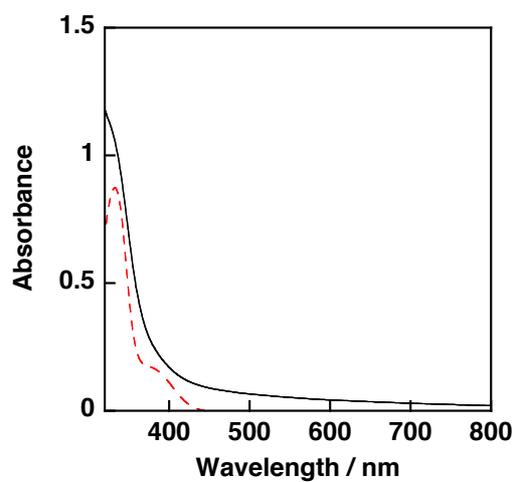


Fig. S1 UV-vis absorption spectra of 0.5 mM QuPh⁺-NA ion (red broken) in MeCN and 0.5 mM K₂PtCl₆ (black solid) in water.



Fig. S2 A photograph of a dispersion MeCN solution containing QuPh⁺-NA@sAIMCM-41 and oxalate anion after photoirradiation ($\lambda > 340$ nm) in the presence of 0.5 mM Cu(NO₃)₂.