

Nanofabrication of a Solid-State, Mesoporous Nanoparticle Composite for Efficient Photocatalytic Hydrogen Generation

Yusuke Yamada, Hideyuki Tadokoro, Masood Naqshbandi, John Canning, Maxwell J. Crossley, Tomoyoshi Suenobu and Shunichi Fukuzumi

Citation	ChemPlusChem, 81(6): 521-525
Issue Date	2016-06-16
Type	Journal Article
Textversion	author
Rights	This is the peer reviewed version of the following article: YAMADA, Y., TADOKORO, H., NAQSHBANDI, M., CANNING, J., CROSSLEY, M. J., SUENOBU, T., & FUKUZUMI, S. (2016). Nanofabrication of a Solid-State, Mesoporous Nanoparticle Composite for Efficient Photocatalytic Hydrogen Generation. ChemPlusChem. 81, 521-525. , which has been published in final form at https://doi.org/10.1002/cplu.201600148 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.
DOI	10.1002/cplu.201600148

Self-Archiving by Author(s)
Placed on: Osaka City University Repository

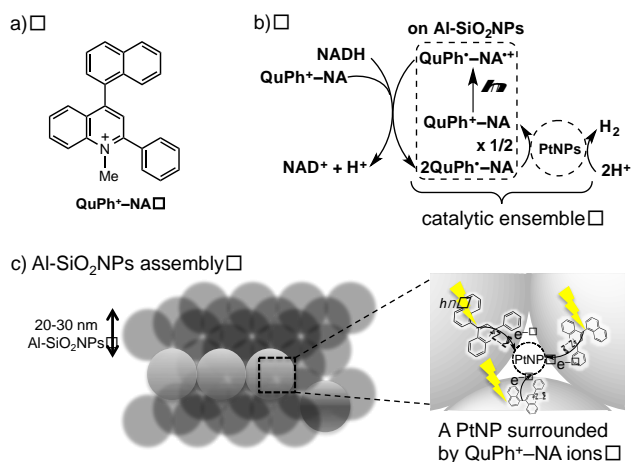
Nanofabrication of Solid-State, Mesoporous Nanoparticle Composite for Efficient Photocatalytic Hydrogen Generation**

Yusuke Yamada,* Hideyuki Tadokoro, Masood Naqshbandi, John Canning,* Maxwell J. Crossley,* Tomoyoshi Suenobu, and Shunichi Fukuzumi*

Abstract: Room temperature self-assembly is used to fabricate a periodic array of uniformly sized Al^{3+} -doped SiO_2 nanoparticles ($\text{Al-SiO}_2\text{NPs}$, 20–30 nm). The uniform mesoporous structure is suitable for uniformly incorporating and distributing Pt nanoparticles (PtNPs), which are used as hydrogen evolution catalysts in artificial photosynthetic systems, without agglomeration during the catalytic reaction. When the surfaces of the $\text{Al-SiO}_2\text{NPs}$ are covered with an organic photocatalyst (2-phenyl-4-(1-naphthyl)quinolinium ion, QuPh^+-NA), each PtNP is surrounded by multiple QuPh^+-NA ions. The structure allows the PtNP to receive multiple electrons from QuPh^+-NA molecules, which are generated by reduction of the photoexcited state of QuPh^+-NA ions ($\text{QuPh}^+-\text{NA}^{*+}$) with β -dihydronicotinamide adenine dinucleotide (NADH), resulting in efficient photocatalytic H_2 evolution.

Artificial photosynthesis attracts many researchers to realize an energy-sustainable society based on solar energy.^[1–3] For producing hydrogen (H_2) as a solar fuel, two different approaches have been developed. One is a heterogeneous approach in which semiconductors are used as photocatalysts.^[4] This type of catalyst

involves inherent problems with tuning the electronic bandgap suitable for visible light absorption. The other is a homogeneous approach using multiple components of light-harvesting, charge-separation, and catalysis units, which can be developed and optimized separately.^[5–13] This approach allows the use of various types of photosensitizers, which absorb visible light, with metal nanoparticles (MNPs) such as PtNPs as H_2 -evolution catalysts. Among models mimicking light harvesting and charge-separation units,^[14–16] a class of donor-acceptor linked cation molecules such as 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh^+-NA , Scheme 1a)^[16] have been reported to afford an extremely long-lived electron-transfer (ET) state with high oxidation and reduction abilities under photoirradiation. QuPh^+-NA successfully acts as an organic



[*] Prof. Dr. Yusuke Yamada
Department of Applied Chemistry and Bioengineering,
Graduate School of Engineering, Osaka City University,
Osaka 558-8585 (Japan)
E-mail: ymd@a-chem.eng.osaka-cu.ac.jp

Hideyuki Tadokoro, and Prof. Dr. Tomoyoshi Suenobu
Department of Material and Life Science, Graduate School
of Engineering, ALCA and SENTAN, Japan Science and
Technology Agency (JST), Osaka University
2-1 Yamada-oka, Suita, Osaka 565-0871 (Japan)

Masood Naqshbandi, and Prof. Dr. Maxwell J. Crossley
School of Chemistry, The University of Sydney, Sydney,
New South Wales 2006 (Australia)
m.crossley@sydney.edu.au

Prof. Dr. John Canning
interdisciplinary Photonics Laboratories, School of
Chemistry, The University of Sydney, Sydney,
New South Wales 2006 (Australia)
E-mail: john.canning@sydney.edu.au

Prof. Dr. Shunichi Fukuzumi
Department of Chemistry and Nano Science
Ewha Womans University, Seoul 120-750 (Korea)
Faculty of Science and Engineering, Meijo University,
Nagoya, Aichi 468-0073 (Japan)
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

[**] This work was supported by ALCA and SENTAN projects
from JST (to S.F.) and JSPS KAKENHI (Grant Nos.
24350069 and 15K14223 to Y.Y.).

Supporting information for this article is available on the
WWW under <http://www.angewandte.org> or from the au-
thor.

Scheme 1. a) Chemical structure of QuPh^+-NA ion, b) overall photocatalytic cycle of the H_2 -evolution system and c) catalytic structure prepared by mixing and dried silica-alumina nanoparticles ($\text{Al-SiO}_2\text{NPs}$) supporting QuPh^+-NA on silica-alumina and PtNPs.

photocatalyst for efficient photocatalytic H_2 evolution together with PtNPs and β -dihydronicotinamide adenine dinucleotide (NADH) in solution.^[17–19] As indicated in Scheme 1b, photoexcited QuPh^+-NA ($\text{QuPh}^+-\text{NA}^{*+}$) reacts with NADH to form QuPh^+-NA , which injects an electron to PtNPs for H_2 evolution.^[17–19] The long lifetime of the ET state resulted in elimination of an electron relay, which is usually a necessary component of photocatalytic H_2 -evolution systems for elongation of the lifetime of the charge-separated state.

The lifetime of the ET states of QuPh^+-NA generated by photoirradiation can be further elongated ($\tau > 20$ s) by being loaded on silica-alumina, where a QuPh^+-NA molecule cannot interact with any other molecule.^[20] Additionally, the loading of PtNPs on silica-alumina can be expected to suppress deactivation and agglomeration or clustering of PtNPs during a reaction.^[21] However, conventional silica-alumina loading QuPh^+-NA and PtNPs exhibited only moderate catalytic activity,^[22] mainly because of a disordered structure unsuitable for multiple electron reduction. Each PtNP should be surrounded by multiple QuPh^+-NA ions on a support for more efficient photocatalytic H_2 evolution.

Recently, room temperature self-assembly of monodispersed SiO₂ nanoparticles (20-30 nm) has been reported to form a densely packed monolithic structure with discrete mesospaces (2-6 nm) among the particles by convective flow through evaporation.^[23] This assembly contains discrete and uniform mesospaces, which can stably incorporate not only various organic molecules including organic dyes such as Rhodamine B, zinc porphyrins^[24] but also enzymes.^[25] The discrete mesospaces of the assembly act as molecular sieves and aggregation and clustering of incorporated PtNPs will be strongly avoided. Additionally, an ideal catalytic ensemble for photocatalytic H₂ evolution can be obtained when a single PtNP is incorporated in a discrete mesospace, and the wall of the mesospace is decorated by the QuPh⁺-NA ions (Scheme 1c). The self-assembly of the SiO₂ nanoparticles using as the support assures the high dispersion and uniform catalytic ensemble formation in the mesospaces. However, PtNPs and QuPh⁺-NA have yet to be incorporated into the assembly.

We report herein the construction of self-assembled structures of size-controlled Pt nanoparticles (PtNPs) capped with polyvinyl pyrrolidone (PVP) and Al³⁺-doped SiO₂ nanoparticles uniform in size 20-30 nm (Al-SiO₂NPs) incorporating QuPh⁺-NA for the efficient photocatalytic H₂ evolution using NADH as a sacrificial electron donor. Doping of Al³⁺ ions to SiO₂ generates cation exchange sites at the surfaces, where cationic QuPh⁺-NA can be stably adsorbed. The PtNPs capped with PVP have been reported to act as an efficient H₂-evolution catalyst in homogeneous reaction systems.^[19a] The cracked structure of the assembly seems to be advantageous for diffusion of NADH inside the whole volume of the structure.

Al-SiO₂NPs were prepared by surface alumination of SiO₂ nanoparticles with NaAlO₂ in an aqueous dispersion. To the aqueous dispersion of Al-SiO₂NPs, an acetonitrile solution of QuPh⁺-NA and an aqueous suspension of PtNPs (~2 nm) capped with PVP were added successively and placed on an ultrasound sonicator for 30 min. The mixture was then dropped on a glass substrate to form the catalytic structures by slow evaporation in air at room temperature. Figure 1a shows the photograph of obtained black fibers. Thermogravimetric analysis suggested that the catalytic structures incorporated almost all QuPh⁺-NA in the dispersion (Figure S1†). The self-assembled structure of PtNPs and Al-SiO₂NPs was confirmed by TEM measurements as shown in Figure 1b, in which many mesospaces among Al-SiO₂NPs are observed. Incorporation and distribution of PtNPs in the discrete mesospaces were confirmed in the expanded view (Figure 1b, inset). The size uniformity of the mesospaces in the assembly was confirmed by N₂ adsorption-desorption isotherms measurement at 77 K (Figure 1c), which is a method used previously in combination with atomic force microscopy to confirm that it is uniform throughout the volume of the structure.^[23] The isotherm is clearly classified to type IV, indicating the presence of mesoporous structure.^[26] The pore size distribution calculated from the adsorption branch of the isotherms by the Barrett-Joyner-Halenda (BJH) method, which assumes a cylindrical pore model, was determined to be $R = \sim 6$ nm with a Brunauer-Emmett-Teller (BET) surface area as low as 132 m² g⁻¹ (Figure 1d). Although the mesospaces in the structure are not the cylindrical pore assumed in the BJH model, the narrower pore size distribution assures the uniformity of the mesospaces in size. The relatively small surface area in spite of the mesoporous structure allows QuPh⁺-NA at low concentrations to almost fully cover the surfaces of the Al-SiO₂NPs, in which each PtNP in a mesospace easily interacts with multiple QuPh⁺-NA ions adsorbed on Al-SiO₂NPs. It also prevents clustering and aggregation that will deleteriously impact electron transfer in the photoresponse involved with catalysis.

Photoresponse of QuPh⁺-NA adsorbed on Al-SiO₂NPs was examined by EPR measurements before the catalytic activity measurements, because the high density of QuPh⁺-NA may

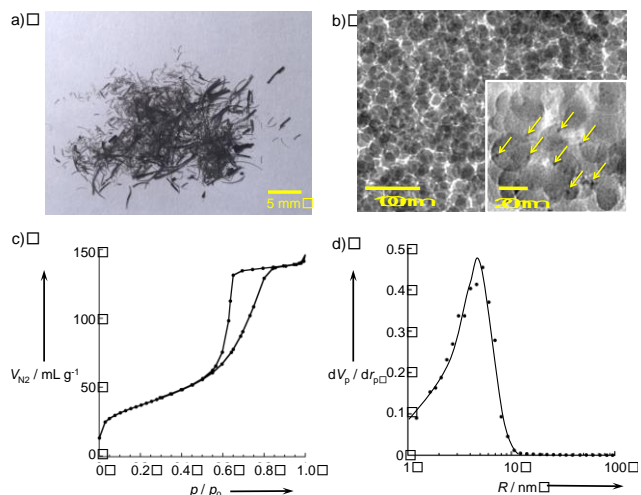


Figure 1. a) A photograph of the catalytic structure of Al-SiO₂NPs incorporating PtNPs and QuPh⁺-NA. b) A transmission electron microscope (TEM) image of the catalytic structures. (The arrows point PtNPs.) c) N₂ adsorption-desorption isotherms of the catalytic structure at 77 K (V_{N₂}: volume of adsorbed N₂ mL mg⁻¹). d) Pore radius (R) distribution calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

promote intermolecular back electron transfer, which shortens the lifetime of the ET state (Figure 2).^[16] Al-SiO₂NPs incorporating QuPh⁺-NA (QuPh⁺-NA/Al-SiO₂NPs) was prepared by the same procedure used for PtNPs/QuPh⁺-NA/Al-SiO₂NPs but without PtNPs. Photoirradiation of QuPh⁺-NA/Al-SiO₂NPs with a 1000 W high-pressure Hg lamp through a UV-band rejection filter (transmission: $\lambda > 340$ nm) leads to the formation of the ET state (QuPh⁺-NA^{•+}) via photoinduced electron transfer from the naphthalene (NA) moiety to the singlet excited state of the quinolinium

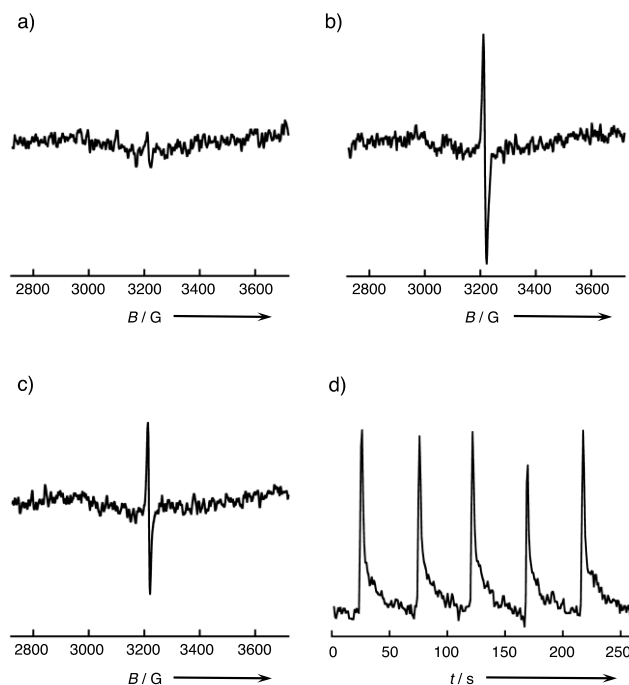


Figure 2. EPR spectra of QuPh⁺-NA/Al-SiO₂NPs (a) in the dark (dry conditions), (b) under illumination ($\lambda > 340$ nm, dry conditions) and (c) under illumination ($\lambda > 340$ nm, wet conditions). (d) Time (t) course of EPR signal intensity of QuPh⁺-NA/Al-SiO₂NPs (wet conditions) under intermittent illumination (light on, 2 sec and light off 48 sec, $\lambda > 340$ nm, wet conditions). (B: magnetic field)

ion (QuPh⁺) moiety. The evidence is the EPR signal appearing at $g = 2.0031$ (Figure 2b),^[20] which was not observed before the photoirradiation (Figure 2a). Water vapor was introduced to the sample at 313 K to examine the effect of water on the formation of the ET state. Appearance of the EPR signal under photoirradiation suggests that the ET state forms in the presence of water. Photorobustness of the QuPh⁺-NA was confirmed by similar peak intensities at repetitive intermittent photoirradiation ON for 2 s followed by 48 s OFF in the dark (Figure 2d).

Photocatalytic H₂ evolution was examined under photoirradiation ($\lambda > 340$ nm) of a phthalate buffer (pH 4.5, 2.0 mL) containing the catalytic structure (PtNPs/QuPh⁺-NA/Al-SiO₂NPs, 5.0 mg; PtNPs, 0.20 $\mu\text{mol}_{\text{Pt}}$; QuPh⁺-NA, 1.1 μmol) and NADH (1.0 mM) at room temperature. The catalytic structure was granulated by magnetic stirring for high dispersion in water before the catalysis measurements. As indicated in Figure 3 (red circle), H₂ evolution lasted for more than 40 h by the successive addition of a condensed aqueous NADH solution to the reaction solution after H₂ evolution ceased. The yields of evolved H₂ based on the

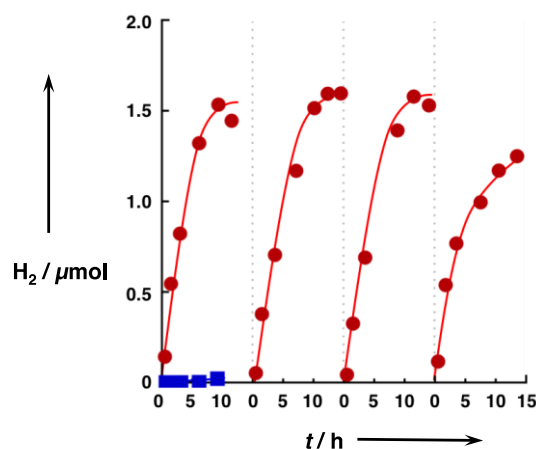


Figure 3. Time (t) courses of H₂ evolution under photoirradiation ($\lambda > 340$ nm) of a de-aerated dispersion (2.0 mL) of a phthalate buffer (pH 4.5) containing the catalytic structure (PtNPs/QuPh⁺-NA/Al-SiO₂NPs, 5.0 mg; Pt, 0.20 $\mu\text{mol}_{\text{Pt}}$; QuPh⁺-NA, 1.1 μmol , red circle) or conventional mesoporous silica-alumina supporting QuPh⁺-NA (5.0 mg, [QuPh⁺-NA]: 1.1 μmol , blue square), PtNPs (Pt: 0.20 μmol) and NADH (1.0 mM). An aliquot (100 μL) of an NADH solution (20 mM) was added to the reaction solution after H₂ evolution ceased.

amount of NADH were 76, 80, 79 and 63% for each run. The initial ($t < 3$ h) H₂-evolution rates normalized by the catalyst weight were $d(\text{H}_2)/dt = 54, 44, 46$ and $52 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$. No obvious structural change was observed by TEM for the catalytic structure after repetitive reactions (Figures S2 and S3[†]). The weight of PtNPs in the reaction suspension was $0.20 \mu\text{mol} \times 195 \text{ g mol}^{-1} = 39 \mu\text{g}$. The mol number of Pt atoms locating on the surfaces of the PtNPs with the size of 2 nm has been reported as $2.8 \times 10^{-3} \text{ mol g}_{\text{Pt}}^{-1}$.^[17b] Thus, the total number of surface Pt atoms is $1.1 \times 10^{-7} \text{ mol}$. The total mol number of evolved H₂ with PtNPs/QuPh⁺-NA/Al-SiO₂NPs was 6.0 μmol , indicating that the turnover number of H₂ evolution per surface Pt atom was 55. Nearly stoichiometric amount of H₂ was evolved when the loading amount of PtNPs in the catalytic structure was increased to 0.40 $\mu\text{mol}_{\text{Pt}}$ with QuPh⁺-NA (0.80 μmol) (Figure S4[†]). On the other hand, negligible amount of H₂ was evolved for the photocatalytic reaction system using the PtNPs and conventional mesoporous silica-alumina incorporating QuPh⁺-NA instead of PtNPs/QuPh⁺-NA/Al-SiO₂NPs under the same reaction conditions (Figure 2, blue square).^[22] The very low H₂ yield resulted from the size of the PtNPs (~2 nm), which is too large to access

photoexcited QuPh⁺-NA incorporated inside the cylindrical mesopores, and the larger surface area unsuitable for close location of PtNPs and QuPh⁺-NA. However, when the same amount of QuPh⁺-NA, PtNPs and NADH were used in a homogeneous system using a mixed solvent of phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)], the stoichiometric amount of H₂ based on the used amount of NADH as a sacrificial electron donor evolved within 2 min.^[19a] Thus, photocatalytic activity of PtNPs/QuPh⁺-NA/Al-SiO₂NPs was decreased for H₂ evolution although no organic solvent is necessary.

The photocatalytic H₂ evolution was also investigated under photoirradiation of a phthalate buffer (pH 4.5) containing PtNPs (0.20 $\mu\text{mol}_{\text{Pt}}$), QuPh⁺-NA/Al-SiO₂NPs (5.0 mg; QuPh⁺-NA, 1.1 μmol), and NADH (1.0 mM) to confirm the catalytic activity originates from the fully pre-assembled structure. A certain amount of H₂ evolution was observed for 6 h with $d(\text{H}_2)/dt = 20 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ (Figure 4, blue square), which is less than half that for fully pre-assembled PtNPs/QuPh⁺-NA/Al-SiO₂NPs (Figure 4, red circle), with 33% H₂ yield. At 2nd run, no increase in the H₂

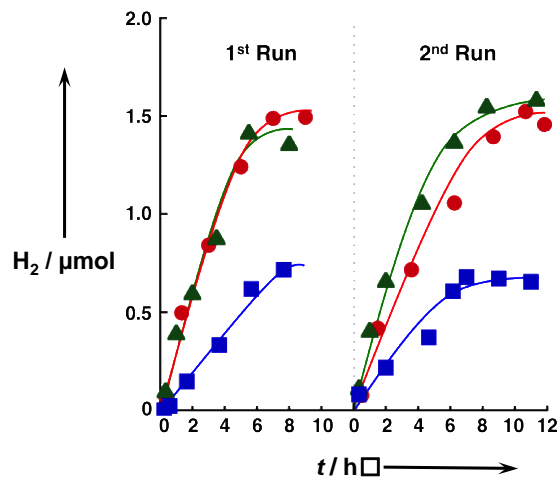


Figure 4. Effect of preparation methods of the catalyst structure on photocatalytic H₂ evolution. Time (t) courses of H₂ evolution under photoirradiation ($\lambda > 340$ nm) of a de-aerated dispersion (2.0 mL) of a phthalate buffer (pH 4.5) containing NADH (1.0 mM), QuPh⁺-NA/Al-SiO₂NPs and a Pt catalyst [K₂PtCl₆ (green triangle) and PtNPs (blue square)]. Red circles are the data obtained for the fully preassembled PtNPs/QuPh⁺-NA/Al-SiO₂NPs for comparison.

yield was observed with a slightly lower H₂-evolution rate ($d(\text{H}_2)/dt = 14 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$). The lower H₂ yields suggest that PtNPs in the solution were hardly accessible to some QuPh⁺-NA molecules located deeply inside the assembly. However, the H₂ yields are significantly high compared with that for the reaction system using the conventional mesoporous silica-alumina as a platform for QuPh⁺-NA (Figure 3, blue square). The larger pore diameter and the cracked structure of QuPh⁺-NA/Al-SiO₂NPs allow large PtNPs to penetrate inside the assembly.

PtNPs can be *in situ* prepared by reduction of K₂PtCl₆, which is accessible to all QuPh⁺-NA ions loaded on the Al-SiO₂ assembly, by utilizing photocatalysis of the QuPh⁺-NA ions under conditions for the photocatalytic H₂ evolution.^[22] The photocatalytic H₂ evolution conducted with the catalytic structure of QuPh⁺-NA/Al-SiO₂NPs in an aqueous phthalate buffer containing K₂PtCl₆ resulted in H₂ yields based on the amount of NADH of 71 and 73% with $d(\text{H}_2)/dt = 46$ and $46 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ in the repetitive experiments (Figure 4, green triangle). The slightly lower H₂ yield in 1st run compared to that in 2nd run resulted from the reduction of the K₂PtCl₆ to PtNPs only in the 1st run. The formation of PtNPs after the photocatalytic reactions was confirmed by TEM observation for the catalyst after H₂ evolution (Figure S3[†]). No particles that

have grown larger than 5 nm was observed because of the size limitation in the mesospaces. The similar H₂-evolution rates for the reaction systems using fully pre-assembled PtNPs/QuPh⁺-NA/Al-SiO₂NPs (Figure 4, red circles) and QuPh⁺-NA/Al-SiO₂NPs and K₂PtCl₆ in the 2nd run suggest that PVP used as an organic capping agent for PtNPs little influenced the catalysis of PtNPs for H₂ evolution.

In summary, we have successfully self-assembled an active catalytic structure of QuPh⁺-NA and PtNPs for photocatalytic H₂ evolution utilizing uniformly distributed mesospaces among Al-SiO₂NPs at room temperature. The mesospaces allowed the controlled incorporation of PtNPs surrounded by multiple QuPh⁺-NA ions. These cannot be well ordered in conventional mesoporous silica-alumina. Self-assembled structures of such metal-oxide nanoparticles are a promising platform to assemble functional organic compounds and nanoparticles.

Experimental Section

All chemicals used for synthesis were obtained from chemical companies and used without further purification. Al-SiO₂NPs were prepared by surface alumination of silica nanoparticles with sodium aluminate at room temperature. PtNPs/QuPh⁺-NA/Al-SiO₂NPs was prepared by slow evaporation of a mixed dispersion containing PtNPs, QuPh⁺-NA and Al-SiO₂NPs. A typical procedure for photocatalytic H₂ evolution is as follows: a dispersion (1.5 mL) of a phthalate buffer (50 mM, pH 4.5) containing PtNPs/QuPh⁺-NA/Al-SiO₂NPs [5.0 mg, QuPh⁺-NA (0.22 mM), [Pt]: 0.05 mM] was magnetically stirred for 3 h in dark. Then, a phthalate buffer containing NADH (4.0 mM, 0.5 mL) was added to the dispersion and flushed with N₂ gas for 10 min before photoirradiation. The solution was then irradiated for a certain time with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a filter (Asahi Techno Glass L39) transmitting $\lambda > 340$ nm at room temperature. The gas in a headspace was analyzed by a gas chromatograph to determine the amount of evolved H₂. The experimental details are described in the Supporting Information.

Acknowledgement

We sincerely acknowledge the Research Center for Ultra-Precision Science & Technology, Osaka University for TEM measurements.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: self-assembly · catalytic ensemble · interparticle mesospaces · spatial arrangement · mesoporous structures

- [1] a) J. M. Thomas, *Energy Environ. Sci.* **2014**, 7, 19; b) Z. Han, R. Eisenberg, *Acc. Chem. Res.* **2014**, 47, 2537; c) S. Fukuzumi, K. Ohkubo, T. Suenobu, *Acc. Chem. Res.* **2014**, 47, 1455.
- [2] a) M. D. Kärkäs, E. V. Johnston, O. Verho, B. Åkermark, *Acc. Chem. Res.* **2014**, 47, 100; b) J. R. McKone, N. S. Lewis and H. B. Gray, *Chem. Mater.* **2014**, 26, 407.
- [3] a) D. G. Nocera, *Acc. Chem. Res.* **2012**, 45, 767; b) M. Wang, L. Chen, L. Sun, *Energy Environ. Sci.* **2012**, 5, 6763.
- [4] a) T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* **2014**, 43, 7520; b) B. Viswanathan, V. Subramanian, J. S. Lee, eds., *Materials and Processes for Solar Fuel Production*, Springer, New York, 2014; c) J. Sa, ed., *Fuel Production with Heterogeneous Catalysis*, CRC Press, Boca Raton, 2014; d) S. J. A. Moriz, S. A. Shevlin, D. J. Martin, Z. X. Guo, J. W. Tang, *Energy Environ. Sci.* **2015**, 8, 731; e) D. Kim, K. K. Sakimoto, D. Hong, P. Yang, *Angew. Chem. Int. Ed.* **2014**, 53, 2.
- [5] a) V. Artero, M. Fontecave, *Chem. Soc. Rev.* **2013**, 42, 2338; b) S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, *Chem. Soc. Rev.* **2014**, 43, 7501; c) D. Z. Zee, T. Chantarojsiri, J. R. Long, C. J. Chang, *Acc. Chem. Res.* **2015**, 48,

- 2027; d) L. Cheng, G. Chen, C.-F. Leung, S.-M. Yiu, C.-C. Ko, E. Anxolabéhère-Mallart, M. Robert, T.-C. Lau, *ACS Catal.* **2015**, 5, 356.
- [6] S. Roy, M. Bacchi, G. Berggren, V. Artero, *ChemSusChem* **2015**, 8, 3632.
- [7] H. Lin, D. Liu, J. Long, Z. Zhang, H. Zhuang, Y. Zheng, X. Wang, *Phys. Chemistry Chem. Phys.* **2015**, 17, 10726.
- [8] T. Zhou, Y. Du, A. Borgna, J. Hong, Y. Wang, J. Han, W. Zhang, R. Xu, *Energy Environ. Sci.* **2013**, 6, 3229.
- [9] (a) M. Zhu, Z. Li, Y. Du, Z. Mou, P. Yang, *ChemCatChem* **2012**, 4, 112. (b) M. Zhu, Y. Dong, Y. Du, Z. Mou, J. Liu, P. Yang, X. Wang, *Chem.–Eur. J.* **2012**, 18, 4367.
- [10] T. Yu, W. Wang, J. Chen, Y. Zeng, Y. Li, G. Yang, Y. Li, *J. Phys. Chem. C* **2012**, 116, 10516.
- [11] T. Arai, S. Matsumoto, N. Obata, T. Kato, N. Nishino, *Photochem. Photobiol. Sci.* **2012**, 11, 289.
- [12] J. Hong, Y. Wang, J. Pan, Z. Zhong, R. Xu, *Nanoscale* **2011**, 3, 4655-4661.
- [13] a) X. Zhang, Z. Jin, Y. Li, S. Li, G. Lu, *J. Phys. Chem. C* **2009**, 113, 2630; b) X. Zhang, Z. Jin, Y. Li, S. Li, G. Lu, *J. Power Sources* **2007**, 166, 74.
- [14] a) A. J. Cowan, J. R. Durant, *Chem. Soc. Rev.* **2013**, 42, 2281; b) S. Fukuzumi, *Curr. Opin. Chem. Biol.* **2015**, 25, 18.
- [15] S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, *J. Am. Chem. Soc.* **2004**, 126, 1600.
- [16] H. Kotani, K. Ohkubo, S. Fukuzumi, *Faraday Discuss.* **2012**, 155, 89.
- [17] a) H. Kotani, K. Ohkubo, Y. Takai, S. Fukuzumi, *J. Phys. Chem. B* **2006**, 110, 24047; b) H. Kotani, R. Hanazaki, K. Ohkubo, Y. Yamada, S. Fukuzumi, *Chem. Eur. J.* **2011**, 17, 2777.
- [18] a) S. Fukuzumi, Y. Yamada, T. Suenobu, K. Ohkubo, H. Kotani, *Energy Environ. Sci.* **2011**, 4, 2754; b) S. Fukuzumi, D. Hong, Y. Yamada, *J. Phys. Chem. Lett.* **2013**, 4, 3458.
- [19] a) Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo, S. Fukuzumi, *J. Am. Chem. Soc.* **2011**, 133, 16136; b) Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo, S. Fukuzumi, *Energy Environ. Sci.* **2012**, 5, 6111; c) Y. Yamada, T. Miyahigashi, K. Ohkubo, S. Fukuzumi, *Phys. Chem. Chem. Phys.* **2012**, 14, 10564.
- [20] Y. Yamada, A. Nomura, K. Ohkubo, T. Suenobu, S. Fukuzumi, *Chem. Commun.* **2013**, 49, 5132.
- [21] Y. Yamada, S. Shikano, S. Fukuzumi, *J. Phys. Chem. C* **2013**, 117, 13143.
- [22] a) Y. Yamada, H. Tadokoro, S. Fukuzumi, *RSC Adv.*, **2013**, 3, 25677; b) Y. Yamada, A. Nomura, H. Tadokoro, S. Fukuzumi, *Catal. Sci. Technol.* **2015**, 5, 428.
- [23] J. Canning, M. Ma, B. C. Gibson, J. Shi, K. Cook, M. J. Crossley, *Opt. Mater. Express* **2013**, 3, 2028.
- [24] a) M. Naqshbandi, J. Canning, B. C. Gibson, M. M. Nash, M. J. Crossley, *Nat. Commun.* **2012**, 3, 1188; b) J. Canning, G. Huyang, M. Ma, A. Beavis, D. Bishop, K. Cook, A. McDonagh, D. Shi, G.-D. Peng, M. J. Crossley, *Nanomaterials* **2014**, 4, 157.
- [25] T. Y. Nara, H. Togashi, S. Ono, M. Egami, C. Sekikawa, Y. Suzuki, I. Masuda, J. Ogawa, N. Horinouchi, S. Shimizu, F. Mizukami, T. Tsunoda, *J. Mol. Catal. B* **2011**, 68, 181.
- [26] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* **1985**, 57, 603.

Entry for the Table of Contents

Photocatalysis

Yusuke Yamada,* Hideyuki Tadokoro,
Masood Naqshbandi, John Canning,*
Maxwell J. Crossley,* Tomoyoshi Sue-
nobu, and Shunichi Fukuzumi* _____ **Page – Page**

An assembly of nearly monodispersed Al^{3+} -doped SiO_2 nanoparticles (20-30 nm) possessing interparticle mesospaces is suitable for incorporating Pt nanoparticles and an organic photocatalyst (2-phenyl-4-(1-naphthyl)quinolinium ion) acts as an efficient composite catalyst for photocatalytic H_2 evolution.

