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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\textsuperscript{3+}-doped SiO\textsubscript{2} nanoparticles (Al-SiO\textsubscript{2} 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 Al-SiO\textsubscript{2} NPs are covered with an organic photocatalyst (2-phenyl-4-(1-naphthyl)quinolinium ion, QuPh\textsuperscript{+}–NA), each PtNP is surrounded by multiple QuPh\textsuperscript{+}–NA ions. The structure allows the PtNP to receive multiple electrons from QuPh\textsuperscript{+}–NA molecules, which are generated by reduction of the photoexcited state of QuPh\textsuperscript{+}–NA ions (QuPh\textsuperscript{+}–NA\textsuperscript{–}) with \(\beta\)-dihydronicotinamide adenine dinucleotide (NADH), resulting in efficient photocatalytic \(\text{H}_2\) evolution.

Artificial photosynthesis attracts many researchers to realize an energy-sustainable society based on solar energy.\textsuperscript{[1–3]} For producing hydrogen (\(\text{H}_2\)) as a solar fuel, two different approaches have been developed. One is a heterogeneous approach in which semiconductors are used as photocatalysts.\textsuperscript{[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.\textsuperscript{[5–13]} This approach allows the use of various types of photosensitizers, which absorb visible light, with metal nanoparticles (MNPs) such as PtNPs as \(\text{H}_2\)-evolution catalysts. Among models mimicking light harvesting and charge-separation units,\textsuperscript{[14–16]} a class of donor-acceptor linked cation molecules such as 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh\textsuperscript{+}–NA, Scheme 1a)\textsuperscript{[16]} have been reported to afford an extremely long-lived electron-transfer (ET) state with high oxidation and reduction abilities under photoradiation. QuPh\textsuperscript{+}–NA successfully acts as an organic photocatalyst for efficient photocatalytic \(\text{H}_2\) evolution together with PtNPs and \(\beta\)-dihydronicotinamide adenine dinucleotide (NADH) in solution.\textsuperscript{[17–19]} As indicated in Scheme 1b, photoexcited QuPh\textsuperscript{+}–NA (QuPh\textsuperscript{+}–NA\textsuperscript{–}) reacts with NADH to form QuPh\textsuperscript{+}–NA, which injects an electron to PtNPs for \(\text{H}_2\) evolution.\textsuperscript{[17–19]} The long lifetime of the ET state resulted in elimination of an electron relay, which is usually a necessary component of photocatalytic \(\text{H}_2\)-evolution systems for elongation of the lifetime of the charge-separated state.

The lifetime of the ET states of QuPh\textsuperscript{+}–NA generated by photoradiation can be further elongated (\(\tau > 20\) s) by being loaded on silica-alumina, where a QuPh\textsuperscript{+}–NA molecule cannot interact with any other molecule.\textsuperscript{[20]} Additionally, the loading of PtNPs on silica-alumina can be expected to suppress deactivation and agglomeration or clustering of PtNPs during a reaction.\textsuperscript{[21]} However, conventional silica-alumina loading QuPh\textsuperscript{+}–NA and PtNPs exhibited only moderate catalytic activity,\textsuperscript{[22]} mainly because of a disordered structure unsuitable for multiple electron reduction. Each PtNP should be surrounded by multiple QuPh\textsuperscript{+}–NA ions on a support for more efficient photocatalytic \(\text{H}_2\) evolution.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
Recently, room temperature self-assembly of monodispersed SiO₂ nanoparticles (20-30 nm) has been reported to form a densely packed monolithic structure with discrete mesopores (2-6 nm) among the particles by convective flow through evaporation.  

This assembly contains discrete and uniform mesopores, which can stably incorporate not only various organic molecules including organic dyes such as Rhodamine B, zinc porphyrin but also enzymes. The discrete mesopores 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 mesopore, and the wall of the mesopore 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 mesopores. 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 Al⁻³-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 Al⁺ 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. 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 aluminization 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 mesopores among Al-SiO₂NPs are observed. Incorporation and distribution of PtNPs in the discrete mesopores were confirmed in the expanded view (Figure 1b, inset). The size uniformity of the mesopores 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. The isotherm is clearly classified to type IV, indicating the presence of mesoporous structure. 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 = ~6 nm with a Brunauer-Emmett-Teller (BET) surface area as low as 132 m² g⁻¹ (Figure 1d). Although the mesopores in the structure are not the cylindrical pore assumed in the BJH model, the narrower pore size distribution assures the uniformity of the mesopores 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 mesopore 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 photoreaction 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 promote intermolecular back electron transfer, which shortens the lifetime of the ET state (Figure 2). 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-bank rejection filter (transmission: λ > 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.
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. Photoeasusess 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 \(\mathrm{H}_2\) evolution was examined under photoirradiation (\(\lambda > 340\) nm) of a de-aerated dispersion (2.0 mL) of a phthalate buffer (pH 4.5, 20 mM) containing the catalytic structure (PtNPs/QuPh\(^+\)--NA/Al-SiO\(_2\)NPs, 5.0 mg; PtNPs, 0.20 \(\mu\)mol Pt; QuPh\(^+\)--NA, 1.1 \(\mu\)mol) 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), \(\mathrm{H}_2\) evolution lasted for more than 40 h by the successive addition of a condensed aqueous NADH solution to the reaction solution after \(\mathrm{H}_2\) evolution ceased. The yields of evolved \(\mathrm{H}_2\) based on the amount of NADH were 76, 80, 79 and 63% for each run. The initial \((t < 3\) h) \(\mathrm{H}_2\)-evolution rates normalized by the catalyst weight were \(d(\mathrm{H}_2)/dt = 54, 44, 46\) and 52 \(\mu\)mol \(\cdot\) g\(_{\text{cat}}\)\(^{-1}\). No obvious structural change was observed by TEM for the catalytic structure after repetitive reactions (Figures S2 and S3\(^{[3]}\)). The weight of PtNPs in the reaction suspension was 0.20 \(\mu\)mol Pt \times 195 g \(\mu\)mol\(^{-1}\) = 39 \(\mu\)g. The total number of Pt atoms located on the surfaces of the PtNPs with the size of 2 nm has been reported as 2.8 \times 10\(^7\) \(\mu\)mol \(\cdot\) g\(_{\text{Pt}}\)\(^{-1}\). Thus, the total number of surface Pt atoms is 1.1 \times 10\(^7\) \(\mu\) mol. The total mol number of evolved \(\mathrm{H}_2\) with PtNPs/QuPh\(^+\)--NA/Al-SiO\(_2\)NPs was 6.0 \(\mu\)mol, indicating that the turnover number of \(\mathrm{H}_2\) evolution per surface Pt atom was 55. Nearly stoichiometric amount of \(\mathrm{H}_2\) was evolved when the loading amount of PtNPs in the catalytic structure was increased to 0.40 \(\mu\)mol Pt with QuPh\(^+\)--NA (0.80 \(\mu\)mol) (Figure S4\(^{[4]}\)). On the other hand, negligible amount of \(\mathrm{H}_2\) was evolved for the photocatalytic reaction system using the PtNPs and conventional mesoporous silica-alumina incorporating QuPh\(^+\)--NA instead of PtNPs/QuPh\(^+\)--NA/Al-SiO\(_2\)NPs under the same reaction conditions (Figure 2, blue square).\(^{[22]}\) The very low \(\mathrm{H}_2\) yield resulted from the size of the PtNPs (2 nm), which is too large to access the size of the PtNPs (~2 nm), which is too large to access the surfaces of the PtNPs with the size of 2 nm has been reported as 2.8 \times 10\(^7\) \(\mu\)mol \(\cdot\) g\(_{\text{Pt}}\)\(^{-1}\). Thus, the total number of surface Pt atoms is 1.1 \times 10\(^7\) \(\mu\) mol. The total mol number of evolved \(\mathrm{H}_2\) with PtNPs/QuPh\(^+\)--NA/Al-SiO\(_2\)NPs was 6.0 \(\mu\)mol, indicating that the turnover number of \(\mathrm{H}_2\) evolution per surface Pt atom was 55. 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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 \(\mathrm{H}_2\) 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-SiO\(_2\)NPs was decreased for \(\mathrm{H}_2\) evolution although no organic solvent is necessary.

The photocatalytic \(\mathrm{H}_2\) evolution was also investigated under photoirradiation of a phthalate buffer (pH 4.5) containing PtNPs (0.20 \(\mu\)mol Pt), QuPh\(^+\)--NA/Al-SiO\(_2\)NPs (5.0 mg; QuPh\(^+\)--NA, 1.1 \(\mu\)mol), and NADH (1.0 mM) to confirm the catalytic activity originates from the fully pre-assembled structure. A certain amount of \(\mathrm{H}_2\) evolution was observed for 6 h with \(d(\mathrm{H}_2)/dt = 20 \mu\)mol \(\cdot\) h\(^{-1}\) \(\cdot\) g\(_{\text{cat}}\)\(^{-1}\) (Figure 4, blue square), which is less than half that for fully pre-assembled PtNPs/QuPh\(^+\)--NA/Al-SiO\(_2\)NPs (Figure 4, red circle), with 33% \(\mathrm{H}_2\) yield. At 2nd run, no increase in the \(\mathrm{H}_2\) yield was observed with a slightly lower \(\mathrm{H}_2\)-evolution rate (\(d(\mathrm{H}_2)/dt = 14 \mu\)mol \(\cdot\) h\(^{-1}\) \(\cdot\) g\(_{\text{cat}}\)\(^{-1}\)). The lower \(\mathrm{H}_2\) yields suggest that PtNPs in the solution were hardly accessible to some QuPh\(^+\)--NA molecules located deeply inside the assembly. However, the \(\mathrm{H}_2\) 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-SiO\(_2\)NPs allow PtNPs to penetrate inside the assembly.

PtNPs can be in situ prepared by reduction of K\(_2\)PtCl\(_6\), which is accessible to all QuPh\(^+\)--NA ions loaded on the Al-SiO\(_2\) assembly, by utilizing photocatalysis of the QuPh\(^+\)--NA ions under conditions for the photocatalytic \(\mathrm{H}_2\) evolution.\(^{[22]}\) The photocatalytic \(\mathrm{H}_2\) evolution conducted with the catalytic structure of QuPh\(^+\)--NA/Al-SiO\(_2\)NPs in an aqueous phthalate buffer containing K\(_2\)PtCl\(_6\) resulted in \(\mathrm{H}_2\) yields based on the amount of NADH of 71 and 73% with \(d(\mathrm{H}_2)/dt = 46 \mu\)mol \(\cdot\) h\(^{-1}\) \(\cdot\) g\(_{\text{cat}}\)\(^{-1}\) in the repetitive experiments (Figure 4, green triangle). The slightly lower \(\mathrm{H}_2\) yield in 1st run compared to that in 2nd run resulted from the reduction of the K\(_2\)PtCl\(_6\) to PtNPs only in the 1st run. The formation of PtNPs after the photocatalytic reactions was confirmed by TEM observation for the catalyst after \(\mathrm{H}_2\) evolution (Figure S3\(^{[3]}\)). 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/QuPhe-NA/Al₂SiO₃NPs (Figure 4, red circles) and QuPhe-NA/Al₂SiO₃NPs and K- PtCl₆ 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 QuPhe-NA and PtNPs for photocatalytic H₂ evolution utilizing uniformly distributed mesospaces among Al₂SiO₃NPs at room temperature. The mesospaces allowed the controlled incorporation of PtNPs surrounded by multiple QuPhe-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. Al₂SiO₃NPs were prepared by surface alumination of silica nanoparticles with sodium aluminate at room temperature. PtNPs/QuPhe-NA/Al₂SiO₃NPs was prepared by slow evaporation of a mixed dispersion containing PtNPs, QuPhe-NA and Al₂SiO₃NPs. 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/QuPhe-NA/Al₂SiO₃NPs [5.0 mg, QuPhe-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 λ > 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.

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An assembly of nearly monodispersed Al³⁺-doped SiO₂ 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 H₂ evolution.