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Metal-free hydrogen evolution with nanoparticles derived from pyrene *via* two-photon ionization induced by laser irradiation†

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Laser irradiation of a cyclohexane solution containing pyrene resulted in hydrogen evolution as pyrene was converted to a metal-free nanoparticle photocatalyst. When C₆H₁₂ was replaced by C₆D₁₂, D₂ was mainly evolved. This result suggests that the hydrogen source is cyclohexane used as a solvent. Photocatalytic hydrogen evolution was also observed in an aqueous solution by using a water-soluble pyrene derivative.

Various approaches for light energy conversion into chemical energy have been developed in artificial photosynthesis.^{1–4} Heterogeneous metallic nanoparticles composed of semiconductor metallic oxides have been widely used for water splitting as catalysts in hydrogen production from water.^{5–8} However, the catalytic mechanism of hydrogen evolution is yet to be clarified. On the other hand, molecular metal-free photocatalysis under homogeneous conditions has recently gained special attention in organic synthesis, physical chemistry and green chemistry because of its low cost and mild reaction conditions for activation of substrates.^{9–13} Preparation of organic nanocrystals has been established by laser induced decomposition of organic crystals and particles.^{14–18} However, there have been few reports on photocatalytic reactions using heterogeneous organic nanoparticles as metal-free photocatalysts.^{19,20}

Pyrene is known as an organic photosensitizer in the photochemical reactions. Two-photon excitation of pyrene produces photoionization products, the pyrene radical cation and a solvated electron under homogeneous conditions. The one-electron oxidation

and reduction potential of pyrene is +1.3 and –2.0 V vs. SCE in MeCN.^{21,22} The pyrene radical anion is generated by two-photon excitation and one-electron reduction by the solvated electron [e[–](solv)] or photoinduced electron transfer between the excited state of a pyrene molecule (S2 or S1 state) and the ground state of another pyrene molecule due to the higher-lying excited state ($E(S1) = 3.34$ eV)^{23–26} than the HOMO–LUMO gap (3.30 eV) in polar solvent. In nonpolar solvent, the solvated electron may have strong reducing ability to reduce a proton (H⁺) to hydrogen (H₂) without a metal catalyst.

H₂ is primarily used in the chemical industry as a reactant and is proposed as an alternative energy source for the future. Catalytic H₂ evolution systems have extensively been studied by using sacrificial electron donors, photosensitisers and electron mediators such as methyl viologen and an H₂ evolution catalyst such as platinum.^{27–32} However, there has been no report on photocatalytic H₂ evolution systems *via* proton reduction using an organic photosensitizer alone without any sacrificial electron source.

We report herein that metal-free photoinduced H₂ evolution has been made possible by using pyrene as a precursor for nanoparticles. Efficient H₂ evolution was observed in various organic solvents as well as water using pyrene alone as a metal-free organic photocatalyst under laser light irradiation at room temperature under atmospheric pressure. The reaction mechanism of laser-induced H₂ evolution has been clarified based on the oxidized products, deuterium kinetic isotope effects and the dependence of the rate of H₂ evolution on the laser intensity.

Nanosecond laser flash irradiation ($\lambda = 355$ nm, 10 Hz, 40 mJ pulse^{–1}, i.d. 8 mm) of a deaerated cyclohexane solution containing pyrene (50 mM) for 90 min resulted in the formation of highly dispersed black nanoparticles in the solution. Fig. 1 shows the UV-vis absorption spectral change upon laser irradiation of pyrene in cyclohexane. The characteristic absorption bands at 306, 319 and 334 nm due to pyrene observed before irradiation disappeared and turned to the broad absorption from the UV-vis to near-IR region.

To characterize the nanoparticles, dynamic light scattering (DLS) measurements were performed for the photochemically

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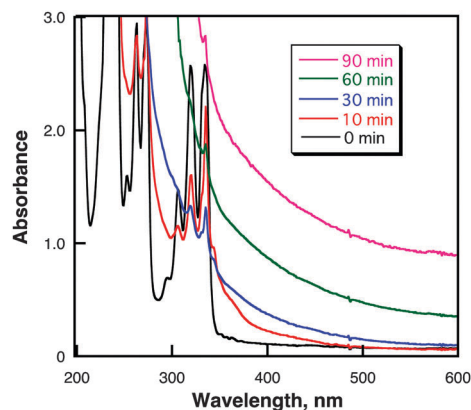


Fig. 1 UV-vis absorption spectral changes for growing pyrene nanoparticles observed in a cyclohexane solution (2.5 mL) containing pyrene (50 μ M) under laser irradiation (λ = 355 nm; 40 mJ pulse⁻¹; 10 pulse s⁻¹).

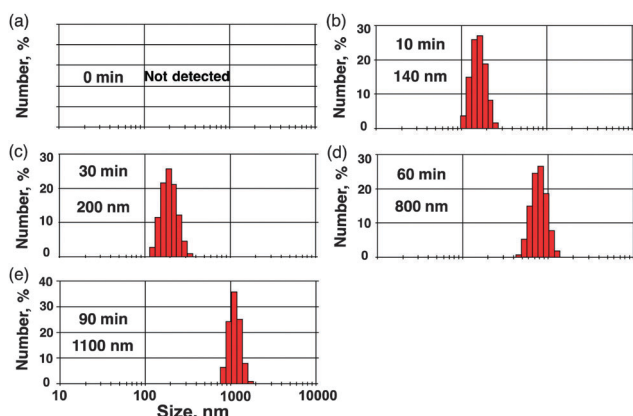


Fig. 2 Time course of DLS data of a cyclohexane solution (2.5 mL) containing pyrene (50 μ M) under laser irradiation (λ = 355 nm; 40 mJ pulse⁻¹; 10 Hz).

growing nanoparticles. The nanoparticles of 420 nm size were observed after laser irradiation for 30 min as shown in Fig. 2a.

The particle size grows by further laser irradiation to afford nanoparticles of 1100 nm size after the irradiation time of 90 min. Transmission electron microscopy (TEM) measurements were performed to evaluate the transformation of pyrene nanoparticles after laser irradiation. TEM images after photoirradiation for 30 min (Fig. 3a and b) clearly exhibit small nanoparticles. After irradiation for 90 min, the size of nanoparticles was enlarged (Fig. 3c and d). The IR spectra of nanoparticles showed that the characteristic peak at 3043 cm⁻¹ due to the C-H vibration disappeared and it was blue-shifted to 2925 cm⁻¹ with an increase in irradiation time (see Fig. S1 in the ESI[†]). This suggests that C-H bonds of pyrene were broken in growing nanoparticles. To obtain the information of the C-H bond of pyrene in the nanoparticle, CHN elemental analysis was performed in growing nanoparticles. The ratio of carbon and hydrogen was 94.4:5.6, which is virtually the same as the comparison of pyrene alone (95.0:5.0). Thus, the main component in the nanoparticle is the undamaged pyrene. The pyrene molecules on the particle surface may be dehydrogenated to form a pyrene polymer by the C-C bond coupling reaction. The formation of pyrene oligomers was confirmed by the powder X-ray diffraction

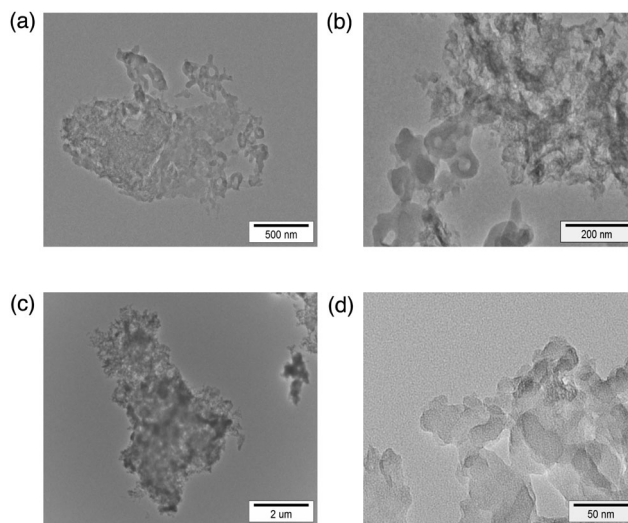
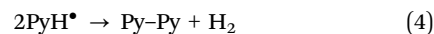
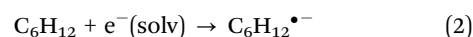
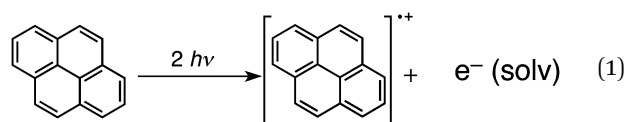


Fig. 3 TEM images of (a) a cyclohexane solution (2.5 mL) of pyrene (50 μ M) after laser light irradiation (λ = 355 nm; 40 mJ pulse⁻¹; 10 pulse s⁻¹) for 30 min, (b) magnified figure of (a), (c) dispersion liquid of precipitation after laser light irradiation (λ = 355 nm; 40 mJ pulse⁻¹; 10 pulse s⁻¹) for 90 min and (d) magnified figure of (c).

(PXRD) measurements (Fig. S2 in the ESI[†]). The XRD patterns with peaks at 2θ = 11 and 24° due to the (001) and (220) planes were maintained after laser irradiation, indicating that the pyrene was not damaged in the nanoparticles.

Laser induced nanoparticle formation was initiated by the photo-ionization of pyrene to form a pyrene radical cation and a solvated electron [eqn (1)]. Hydrogen atom transfer from the cyclohexane radical anion (Cy^{•-}), which is produced by the reduction of cyclohexane by solvated electron [eqn (2)], to the pyrene radical cation (Py^{•+}) occurs to produce a hydrogenated pyrene neutral radical (PyH[•]) and a cyclohexyl radical (C₆H₁₁[•]) [eqn (3)]. Two molecules of PyH[•] react to give the pyrene dimer and H₂ [eqn (4)]. The dimer was detected by MALDI-TOF-MS



measurements (see Fig. S3 in the ESI[†]). The resulting C₆H₁₁[•] is converted to cyclohexene by disproportionation, which was detected by GC-MS analysis (Fig. S4 in the ESI[†]). Butadiene and propene were also detected as side products. The further oligomerization of pyrene occurred by laser irradiation to form the pyrene nano-aggregates.

On the basis of the above-mentioned reaction mechanism in eqn (4), the laser-induced dimerization of pyrene radicals results in H₂ evolution. H₂ evolution was successfully detected by GC experiments in the reaction of pyrene in cyclohexane under nanosecond laser irradiation at 355 nm as shown in Fig. 4. The TON of the



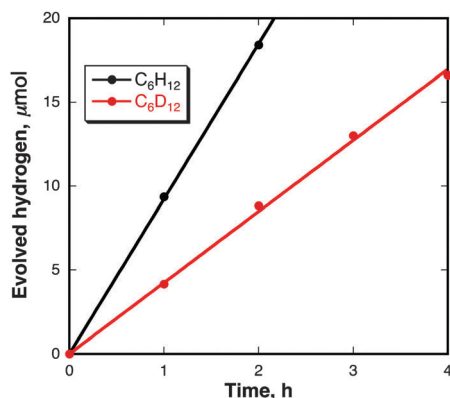


Fig. 4 Time courses of the amount of evolved H_2 and D_2 under laser irradiation ($\lambda = 355 \text{ nm}$; 20 mJ pulse^{-1} ; 10 pulse s^{-1}) of a cyclohexane or cyclohexane- d_{12} solution (2.5 mL) containing pyrene (0.5 mM).

catalysts for H_2 evolution was 2000 for 7 h based on the initial moles of pyrene in cyclohexane where the reaction conditions are $[\text{Py}] = 50 \text{ } \mu\text{M}$, 40 mJ pulse^{-1} at $\lambda = 355 \text{ nm}$ in cyclohexane (2.5 mL). No deactivation was observed in laser irradiation for 7 h (Fig. S5 in the ESI†). When cyclohexane was replaced by cyclohexane- d_{12} as a solvent, D_2 gas was selectively evolved (data are shown in Fig. S6 in the ESI†).³³ The kinetic isotope effect (KIE) value for H_2 evolution was determined to be 2.1. Thus, the rate-determining step of H_2 evolution is carbon-hydrogen bond cleavage of the cyclohexane radical anion by hydrogen atom transfer to the pyrene radical cation. Indeed, no H_2 evolution was observed in cyclohexene instead of cyclohexane (Fig. S7 in the ESI†). H_2 evolution also occurred when the laser light excitation wavelength was changed from 355 nm to 532 nm by an Nd:YAG laser as a light source (Fig. S8 in the ESI†) because pyrene nanoparticles show a strong and broad absorption band covering the whole visible region as previously shown in Fig. 1.

The dependence of the rate of H_2 evolution on the laser intensity was examined using different laser power intensities at 355 nm ($0\text{--}20 \text{ mJ pulse}^{-1}$) as shown in Fig. 5a. The initial rates of H_2 evolution are proportional to the second power of the laser intensity as shown in Fig. 5b. This suggests that an ionization reaction of two-photon absorbed species may be involved in the photocatalytic H_2 evolution. The maximum quantum yield observed was 7.9% when the laser power is 40 mJ pulse^{-1} at 355 nm. The efficiency of the photocatalytic H_2 evolution is affected by the solvent polarities as shown in Table 1. The efficiency of photocatalytic H_2 evolution is highest for cyclohexane and lowest for dimethylsulfoxide in the series of solvents.³⁴ This suggests that electron reducing ability of solvated electron generated by photoionisation of pyrene in non-polar cyclohexane is much higher than in the polar solvent due to the stabilization of solvated electron.

On the basis of the above-mentioned results, the reaction mechanism of photocatalytic H_2 evolution from pyrene nanoparticles (Py-NP) in cyclohexane (CyH) is shown in eqn (5)–(9). Two-photon ionization of Py-NP is much easier than the pyrene monomer, yielding a Py-NP radical cation ($\text{Py-NP}^{\bullet+}$) and a cyclohexane radical anion ($\text{C}_6\text{H}_{12}^{\bullet-}$) [eqn (5)]. Hydrogen atom

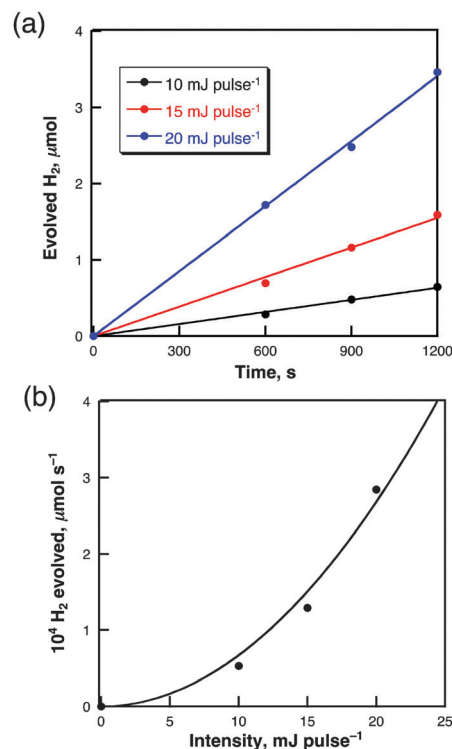


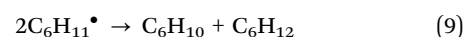
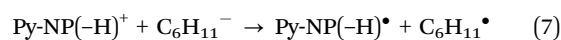
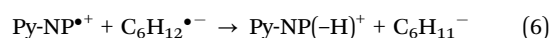
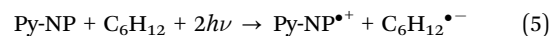
Fig. 5 (a) Time courses of the amount of evolved H_2 in cyclohexane (2.5 mL) containing pyrene particles (0.25 mg) under laser light irradiation ($\lambda = 355 \text{ nm}$; 10, 15 or 20 mJ pulse^{-1} ; 10 pulse s^{-1}) and (b) Plot of the rate of H_2 evolution vs. laser intensity. A fitted line was drawn by a second-order function.

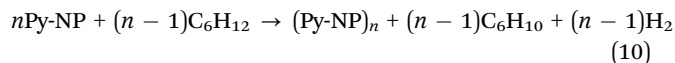
Table 1 Rates of evolved H_2 from Py-NP in various solvents^a

Solvent	Dielectric constant	H_2 ($\mu\text{mol h}^{-1}$)
<i>n</i> -Heptane	1.9	5.7
Cyclohexane	2.0	14
2-Propanol	18	2.6
Acetone	20	3.2
Acetonitrile	37	4.6
Dimethylsulfoxide	47	0.1

^a Conditions: solvent: 2.5 mL; pyrene: 0.50 mM; nanosecond laser ($\lambda = 355 \text{ nm}$; 20 mJ pulse^{-1} ; 10 pulse s^{-1}), under N_2 .

transfer from $\text{C}_6\text{H}_{12}^{\bullet-}$ to $\text{Py-NP}^{\bullet+}$ occurs [eqn (6)], followed by electron transfer from $\text{C}_6\text{H}_{11}^{\bullet-}$ to $\text{Py-NP}(\text{-H})^+$ [eqn (7)] and radical coupling with the release of H_2 [eqn (8)]. Cyclohexyl radicals ($\text{C}_6\text{H}_{11}^{\bullet}$) split disproportionately to yield cyclohexene and cyclohexane [eqn (9)]. The total stoichiometry is given by eqn (10) by summing up eqn (5)–(9).





No nanoparticle of pyrene was formed in an aqueous solution by the laser photoradiation at 355 nm. Thus, no H₂ evolution was observed under photoradiation. When pyrene was replaced by sodium pyrene-1-acetate used as a water-soluble photosensitizer, the nanoparticle formation and H₂ evolution occurred in an aqueous solution under otherwise the same reaction conditions (Fig. S9 in the ESI†). We also examined H₂ evolution using other hydrocarbons instead of pyrene. Nanoparticles were also formed under the same laser-irradiation conditions. Nanoparticles of coronene and 9,10-diphenylanthracene were effective as H₂-evolution photocatalysts. However, the rates of H₂ evolution were 1.4, 1.1 and 0 μmol h⁻¹ for 9,10-diphenylanthracene, coronene and rubrene, respectively, which are significantly lower than the value of pyrene (4.6 μmol h⁻¹) in acetonitrile. In the case of rubrene as a red dye, no nanoparticle was formed without H₂ evolution. It is difficult to form oligomers as precursors of H₂-evolution catalysts because of the more delocalized π-radical cation than pyrene radical cation. In particular, the radical cations of rubrene and 9,10-diphenylanthracene are very stable in solution without any reaction such as dimerization.

In conclusion, pyrene nanoparticles have been demonstrated to act as efficient metal free organic photocatalysts for H₂ evolution from various solvents. Cyclohexane used as a solvent is the most effective hydrogen source in H₂ evolution with pyrene nanoparticles. The rate of H₂ evolution increased with increasing laser intensity, exhibiting a second power dependence, because H₂ was evolved via the two-photon ionization of pyrene followed by hydrogen atom transfer from the cyclohexane radical anion to the pyrene radical cation. Pyrene radical cations dimerise to form oligomer nanoparticles as more effective photocatalysts for H₂ evolution. This is the first report of catalytic H₂ evolution using an organic nanoparticle photocatalyst without inorganic material.

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- HD was formed by the detection with GC as shown in Fig. S6a in the ESI†. HD is a coupling product in the reaction of PyD[•] and PyH[•] [eqn (4)].
- Lower H₂ formation efficiency in more non-polar *n*-heptane than cyclohexane may result from the lower numbers of weak secondary C–H bonds in *n*-heptane.

