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Synergistic effects of Ni and Cu supported on TiO₂ and SiO₂ on photocatalytic H₂ evolution with an electron donor–acceptor linked molecule†

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Synergistic effects of Ni and Cu supported on metal oxides on their catalytic activity for hydrogen evolution were observed in photocatalytic hydrogen evolution with 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh⁺-NA) and β -dihydroneicotinamide adenine dinucleotide (NADH) as a photocatalyst and an electron donor, respectively. Among the catalysts of Ni and Cu supported on TiO₂, SiO₂, SiO₂-Al₂O₃ and CeO₂, Ni and Cu supported on TiO₂ and SiO₂ exhibited high catalytic activity at a wide range of Ni contents [Ni/(Ni + Cu)] from 30% to 70%, while Ni or Cu solely supported on TiO₂ and SiO₂ showed insignificant catalytic activity. The catalytic activity of Ni and Cu supported on TiO₂ and SiO₂ depends on the preparation methods of the catalysts. The catalysts prepared by a co-impregnation method, in which a precursor solution containing both Ni(NO₃)₂ and Cu(NO₃)₂ was used for the impregnation, showed high catalytic activity, whilst catalysts prepared by a sequential impregnation method, in which Ni(NO₃)₂ and Cu(NO₃)₂ were loaded and calcined successively, exhibited low catalytic activity. TEM observations with energy-dispersive X-ray spectroscopy (EDS) elemental mapping of these catalysts revealed that Ni and Cu were closely located on the support surfaces of a catalyst prepared by the co-impregnation method, whereas Ni and Cu were separated in the catalyst prepared by the sequential impregnation method. These results suggest that the close location of Ni and Cu is necessary to exhibit the high catalytic activity. Such a synergistic effect among base metals and metal oxide supports would be a key to develop active catalysts for hydrogen evolution without using platinum group metals.

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Introduction

Hydrogen (H₂) production utilising solar energy attracts much attention from the viewpoint of storage of natural energy as chemical energy.^{1–11} A photocatalytic H₂ evolution system, which mimics natural photosynthesis, can be constructed by using an electron donor, a photosensitiser, an electron mediator and an H₂ evolution catalyst.^{12–20} For example, H₂ evolution can be observed by the photoirradiation of a solution containing ethylenediaminetetraacetic acid disodium salt, [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine), methyl viologen and Pt particles as an electron donor, a photosensitiser, an electron mediator and a hydrogen evolution catalyst, respectively.²¹

This type of H₂ evolution systems requires a sacrificial electron donor; however, a high quantum efficiency and rational improvement in catalysis are achievable by replacing each component after modification.^{8,22,23} As a component of an H₂ evolution catalyst, Pt particles have been most widely used because of their very low overpotential for proton reduction.^{24–26} However, avoiding or reducing the use of Pt metal is strongly demanded because of its high cost and limited supply.^{22,27}

Alternative to Pt nanoparticles (PtNPs), Ru nanoparticles (RuNPs) and Ni nanoparticles (NiNPs) have been demonstrated to act as H₂ evolution catalysts in reaction systems using organic electron donor–acceptor linked dyads as photocatalysts.^{28,29} RuNPs exhibit virtually the same activity as PtNPs; however, the catalytic activity of NiNPs was lower than those of PtNPs and RuNPs.^{28–30} For the improvement of Ni catalysis, concomitant use of other metals such as Cu, Pd and Co is promising as reported for various catalytic reactions.^{31–33} For example, Ni–Cu alloy nanoparticles have been reported to exhibit catalytic activity for thermal H₂ evolution by hydrolysis of sodium borohydride higher than nanoparticles solely composed of Ni or Cu.³⁴ Such a synergistic effect between Ni and Cu has also been reported for

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† Electronic supplementary information (ESI) available: Time courses of H₂ evolution (Fig. S1, S4 and S8), powder X-ray diffraction (Fig. S2, S5 and S9), the amount of H₂ evolved in the repetitive experiments (Fig. S3), diffused reflectance spectra (Fig. S6), and TEM images (Fig. S7). See DOI: 10.1039/c4cy01128g



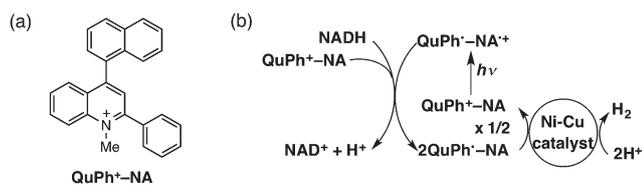
supporting catalysts using SiO_2 ,³⁵ Al_2O_3 ,^{36–38} CeO_2 ,³⁹ ZrO_2 ⁴⁰ and TiO_2 ⁴¹ for high-temperature reactions such as ethanol steam reforming. In general, supporting catalytically active metals on a metal oxide is beneficial for improvements not only in the catalytic activity by metal–support interaction but also in the durability of the metal nanoparticles. However, there have been no systematic studies on the synergistic and support effects of Ni and Cu catalysts on photocatalytic H_2 evolution.

We report herein the H_2 evolution catalysis of Ni–Cu/TiO₂ and Ni–Cu/SiO₂ in an efficient photocatalytic H_2 evolution system composed of a donor–acceptor linked dyad, 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh⁺–NA), as a photocatalyst and β -dihydronicotinamide adenine dinucleotide (NADH) as a sacrificial electron donor. The chemical structure of the organic photocatalyst used in this study and the overall reaction scheme are shown in Scheme 1. Upon photoexcitation of QuPh⁺–NA, electron transfer from the NA moiety to the singlet excited state of the QuPh⁺ moiety occurs to produce the electron-transfer state (QuPh⁺–NA^{•+}).^{42,43} Then, electron transfer from NADH to QuPh⁺–NA^{•+} occurs to produce NADH^{•+} and QuPh⁺–NA.²⁸ NADH^{•+} undergoes deprotonation, releasing one proton to afford NAD[•] that can transfer an electron to QuPh⁺–NA to produce NAD⁺ and QuPh⁺–NA.²⁸ Two equivalents of QuPh⁺–NA thus produced can inject two electrons to Ni–Cu catalysts to evolve H_2 from two protons.²⁸ It should be noted that no electron mediator, which is frequently used in homogeneous photocatalytic H_2 production, is required in the present photocatalytic system because the electron-transfer state of QuPh⁺–NA has a sufficient lifetime for the oxidation of NADH and also for electron injection to Ni–Cu catalysts.^{25,28–30} In this reaction system, effects of the Ni/Cu ratio, preparation methods, the surface area and morphology of SiO₂, and the surface area and crystal structure of TiO₂ on the catalysis of Ni–Cu/TiO₂ and Ni–Cu/SiO₂ for H_2 evolution were examined to clarify the conditions to achieve the synergistic and support effect, which would be a key to develop active catalysts alternative to platinum group metals.

2. Results and discussion

2.1 Photocatalytic H_2 evolution with Ni and a transition metal supported on metal oxides

The effect of concomitant use of Ni with another metal, Cu, Co or Fe, supported on TiO₂ or SiO₂ was examined on the H_2 evolution catalysis of Ni. These catalysts were prepared by a co-impregnation method. Photocatalytic H_2 evolution was



Scheme 1 (a) Structure of QuPh⁺–NA and (b) the overall photocatalytic cycle for H_2 evolution using QuPh⁺–NA and an Ni–Cu catalyst.

performed by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of MeCN and a phthalate buffer (pH 4.5) [1 : 1 (v/v)] containing QuPh⁺–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and TiO₂ or SiO₂ supporting Ni and another metal (M) (100 mg L^{-1} , M = Cu, Co or Fe), in which the loading amount was 1.5 wt% for each of Ni and M, as shown in Fig. 1.

A significant amount of H_2 evolution was observed only for Ni–Cu/TiO₂. TiO₂ is a well-known photocatalyst; however, no H_2 evolution was confirmed for a reaction suspension without QuPh⁺–NA under the present reaction conditions (Fig. S1a†). From the reaction suspension using Ni–Cu/TiO₂ as an H_2 evolution catalyst in the presence of QuPh⁺–NA, continuous H_2 evolution was observed after a short induction period for ca. 5 min. This induction period is for the reduction of NiO, NiCuO₂ and/or Cu₂O species to be catalytically active metallic species because the presence of NiO (JCPDS card no. 78-0643) species in as-prepared Ni–Cu/TiO₂ was confirmed by the diffraction peak around $2\theta = 43.4^\circ$ in the powder X-ray diffraction (Fig. 2). This peak may overlap with the diffraction peaks from NiCuO₂ (JCPDS card no. 6-720) and Cu₂O (JCPDS card no. 05-0667), which have been reported to provide the diffraction peaks at $2\theta = 43.8^\circ$ and 42.5° , respectively, because no diffraction peak was observed at $2\theta = 35.6^\circ$, which indicates formation of CuO (JCPDS card no. 05-0661). Powder XRD measurements were also performed for the Ni–Cu/TiO₂ after the photocatalytic reaction. No diffraction peak indicating formation of Ni⁰ or Cu⁰ species was clearly observed in the peak that appeared around 43° (Fig. S2†).

The initial H_2 evolution rate for the reaction system using Ni–Cu/TiO₂ was determined to be $1.7 \mu\text{mol h}^{-1}$ from the initial (45 min) slope of the reaction system. The apparent quantum yield obtained under photoirradiation ($\lambda = 350 \pm 10$ nm) for 1 h was 1.1%, where the photon flux determined by using an actinometer was 2.89×10^{-9} einstein s^{-1} . The rate was 10 times slower compared with the H_2 evolution rate determined for the reaction system using Pt nanoparticles instead of Ni–Cu/TiO₂, in which the weight of used Pt was the same as that of Ni–Cu in the Ni–Cu/TiO₂; however, the maximum H_2 yield based on the amount of NADH reached as high as 87% ($1.7 \mu\text{mol}$) without using precious metals.

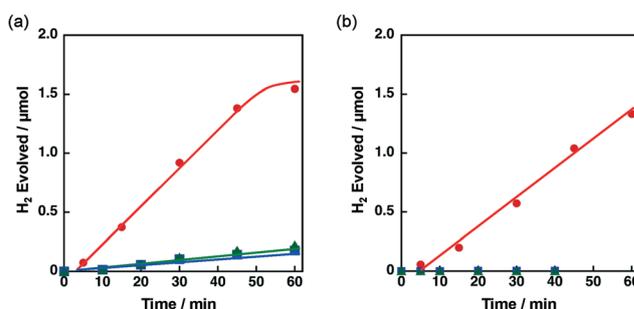


Fig. 1 Time courses of H_2 evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and (a) 3 wt% Ni–M/TiO₂ or (b) 3 wt% Ni–M/SiO₂ (100 mg L^{-1} , M = Cu (red circle), Co (green triangle) and Fe (blue square)).



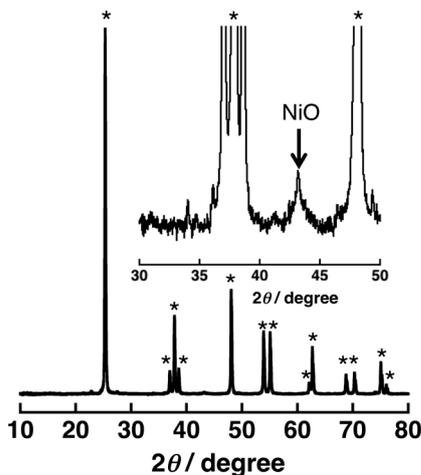


Fig. 2 Powder X-ray diffraction patterns of 3 wt% Ni-Cu/TiO₂ [Ni/Cu = 1:1 (w/w)]. The peaks with the asterisk symbol (*) originate from TiO₂ (anatase).

Ceasing H₂ evolution by cutting off the light in the course of the reaction ensures that the H₂ evolution proceeds photocatalytically (Fig. S1b[†]). In addition, a photocatalytic system using a reduced amount of QuPh⁺-NA (0.11 mM) repeatedly evolved H₂ five times by the addition of NADH to the reaction solution after ceasing H₂ evolution (Fig. S3[†]), and the turnover number based on QuPh⁺-NA reached 21. On the other hand, the amount of H₂ evolution was less than 0.1 μmol from the suspensions containing TiO₂ supporting Ni-Fe and Ni-Co as H₂ evolution catalysts by photoirradiation for 60 min (Fig. 1a, green triangle and blue square, respectively). Similarly, a negligible amount of H₂ evolution was observed from the reaction suspensions containing Ni/TiO₂ and Cu/TiO₂ as the H₂ evolution catalysts (Fig. S4a[†]). Thus, Cu acts as the only suitable counterpart of Ni to achieve synergistic effects on the H₂ evolution catalysis.

Similar synergistic effects of Ni and Cu on the photocatalytic H₂ evolution were observed for Ni-Cu/SiO₂ as shown in Fig. 1b, in which the maximum H₂ yield reached 77% (1.5 μmol) with a H₂ evolution rate of 1.3 μmol h⁻¹ determined from the initial (60 min) slope. No H₂ evolution was confirmed for Ni-Fe/SiO₂ and Ni-Co/SiO₂ by photoirradiation for 40 min. An insignificant amount of H₂ evolution was observed from the reaction suspensions employing Ni/SiO₂ and Cu/SiO₂ as the H₂ evolution catalysts (Fig. S4b[†]). These results obviously indicate that addition of Cu is effective to improve the catalysis of Ni supported on both TiO₂ and SiO₂, although the addition of Fe or Co was unprofitable.

Support effects on the catalytic activity of Ni-Cu catalysts were also examined by employing TiO₂, SiO₂, SiO₂-Al₂O₃ and CeO₂ as supports. Ni and Cu were loaded on the supports by a co-impregnation method where the loading amount was 1.5 wt% for each Cu and Ni. The Brunauer-Emmett-Teller (BET) surface areas of TiO₂, SiO₂, SiO₂-Al₂O₃, and CeO₂ were determined to be 6.8, 52, 118 and 162 m² g⁻¹, respectively. The surface area of the TiO₂ is significantly low compared

to those of others; however, the effect of surface area on the catalytic activity of Ni-Cu/TiO₂ is limited (*vide infra*, Fig. 12). Powder X-ray diffraction patterns of these metal oxides suggested that SiO₂ and SiO₂-Al₂O₃ are amorphous in nature, whilst TiO₂ and CeO₂ are crystalline in the anatase and fluorite structures, respectively (Fig. S5[†]). These metal oxide supports were chosen from those often used for supporting Ni for various reactions.³⁹⁻⁴¹ As mentioned above, both TiO₂ and SiO₂ supporting Ni-Cu showed high catalytic activity in terms of both H₂ yields and H₂ evolution rates (dashed lines in Fig. 3) in the photocatalytic H₂ evolution. On the other hand, Ni-Cu supported on SiO₂-Al₂O₃ (red triangle) and CeO₂ (blue inverted triangle) showed no significant activity for the photocatalytic H₂ evolution as shown in Fig. 3. Although the origin of the support effect is still unclear, the readily reducible nature may be beneficial to produce active sites at the perimeter between Ni-Cu species and the supports. The small negative standard enthalpies of formation for TiO₂ and SiO₂ (-940 and -910 kJ mol⁻¹, respectively) compared to those for CeO₂ and Al₂O₃ (-1089 and -1676 kJ mol⁻¹, respectively) suggest that TiO₂ and SiO₂ are more readily reducible than CeO₂ and SiO₂-Al₂O₃.⁴⁴ Thus, SiO₂ and TiO₂ could be suitable supports to achieve Ni-Cu species that are active for photocatalytic H₂ evolution.

2.2 Effect of preparation methods on H₂ evolution catalysis of Ni-Cu supported on TiO₂ and SiO₂

The catalytic activity of Ni-Cu/TiO₂ and Ni-Cu/SiO₂ was highly influenced by preparation methods. When Ni-Cu/TiO₂ prepared by a co-impregnation method using a solution containing both Cu(NO₃)₂ and Ni(NO₃)₂ was examined for the photocatalytic H₂ evolution, a fast H₂ evolution rate was observed (Fig. 1a, 1.7 μmol h⁻¹). On the other hand, the H₂ evolution rates were as low as 0.5 and 0.3 μmol h⁻¹ with catalysts prepared by a sequential impregnation method, in

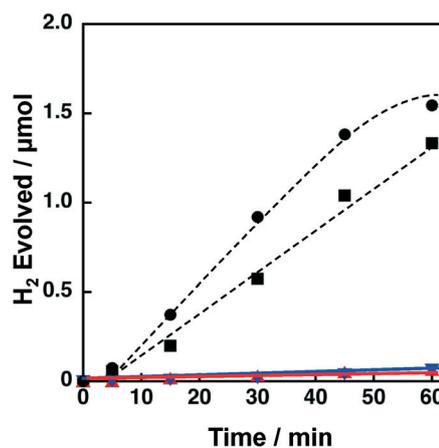


Fig. 3 Time courses of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/MO_x (100 mg L⁻¹, MO_x = TiO₂, circle; SiO₂, square; SiO₂-Al₂O₃, red triangle; CeO₂, blue inverted triangle).



which Ni/TiO₂ was impregnated with a Cu(NO₃)₂ solution or Cu/TiO₂ with a Ni(NO₃)₂ solution (red circle and blue square in Fig. 4a, respectively). Similar influence of preparation methods was also observed for Ni-Cu/SiO₂ as shown in Fig. 4b. The H₂ evolution rate obtained for Ni-Cu/SiO₂ prepared by co-impregnation was significantly larger (Fig. 1b, 1.3 μmol h⁻¹) than those obtained for Ni-Cu/SiO₂ catalysts prepared by the sequential impregnation method, 0.1 and 0.2 μmol h⁻¹.

2.3 Characterisation of Ni-Cu supported on TiO₂ and SiO₂ by UV-vis and TEM with EDS elemental mapping

The Ni-Cu/TiO₂ and Ni-Cu/SiO₂ catalysts prepared by co-impregnation and sequential impregnation methods were characterised by diffuse reflectance UV-vis spectroscopy (DRS). The DRS results of Ni-Cu/TiO₂ catalysts prepared by different procedures are shown in Fig. 5a. Ni-Cu/TiO₂ prepared by the co-impregnation method (red) showed strong absorption in the visible region (400–800 nm) compared with Ni-Cu/TiO₂ catalysts prepared by the sequential impregnation method, with the Cu loaded on Ni/TiO₂ (blue) or Ni loaded on Cu/TiO₂ (green). The peaks that appeared around 600–800 nm in the DRS of Ni-Cu/TiO₂ catalysts differ from superposition of DRS of Ni/TiO₂ and Cu/TiO₂ depicted in Fig. S6a,[†] suggesting that a part of Ni and Cu species have electronic interaction on the TiO₂ surfaces.

A more obvious difference in DRS was observed among Ni-Cu/SiO₂ catalysts prepared by different methods as shown in Fig. 5b. The DRS results of Ni/SiO₂ and Cu/SiO₂ are depicted in Fig. S6b.[†] The DRS of the Ni-Cu/SiO₂ catalyst prepared by the co-impregnation method (red) showed absorption maxima around 480 nm, whereas a small shoulder around 400 nm was observed for the Ni-Cu/SiO₂ catalysts prepared by the sequential impregnation method. The difference in the absorption at the visible region provides the difference in colour. The origin of the brownish colour of the Ni-Cu/SiO₂ catalyst prepared by the co-impregnation method

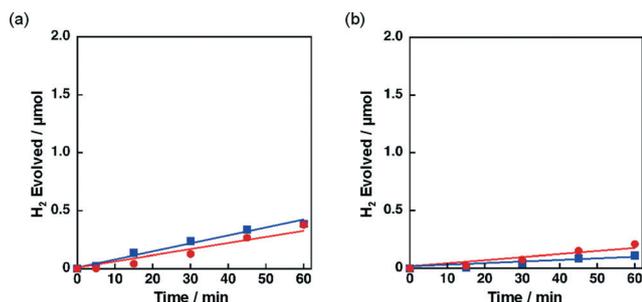


Fig. 4 Time courses of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and (a) 3 wt% Ni-Cu/TiO₂ (100 mg L^{-1}) prepared by a sequential impregnation method (Cu loaded on Ni/TiO₂, red circle, and Ni loaded on Cu/TiO₂, blue square) and (b) 3 wt% Ni-Cu/SiO₂ catalysts (100 mg L^{-1}) prepared by a sequential impregnation (Cu loaded on Ni/SiO₂, red circle, and Ni loaded on Cu/SiO₂, blue square).

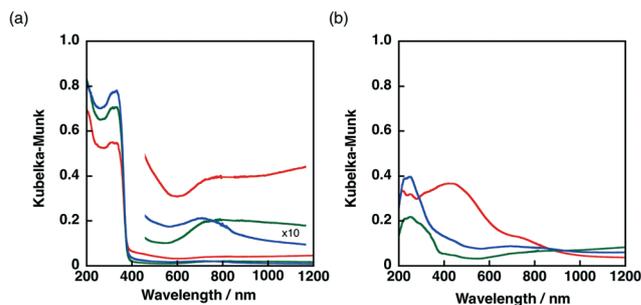


Fig. 5 Diffuse reflectance UV-vis spectra of (a) Ni-Cu/TiO₂ and (b) Ni-Cu/SiO₂ catalysts prepared by co-impregnation (red) and sequential impregnation methods (Cu loaded on Ni/MO₂, blue, and Ni loaded on Cu/MO₂, green. M = Ti or Si).

can be ascribed to the formation of NiCuO₂ on SiO₂ surfaces, which has been proposed for Ni-Cu supported on cordierite in the literature.⁴⁵

The difference in the structures of the Ni-Cu/SiO₂ catalysts prepared by the co-impregnation and the sequential impregnation methods was confirmed by TEM measurements in the atomic level with the energy-dispersive X-ray spectroscopy (EDS) elemental mapping for Si, Cu and Ni. Fig. 6 shows a high-angle annular dark-field scanning TEM (HAADF-STEM) image of particles 20 nm in size formed on Ni-Cu/SiO₂ prepared by the co-impregnation method. The EDS elemental mapping for Si (blue), Cu (red) and Ni (green) indicates that the particle observed in the HAADF-STEM image is composed of both Cu and Ni. On the other hand, the particles on Ni-Cu/SiO₂ prepared by the sequential method, in which Cu was loaded on Ni/SiO₂, showed separated deposition of Cu and Ni. As shown in Fig. 7, comparison of EDS elemental

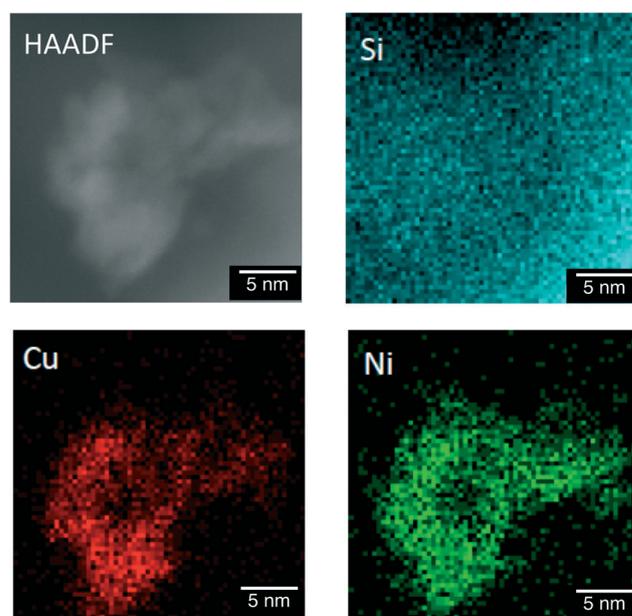


Fig. 6 HAADF-STEM and energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Ni-Cu/SiO₂ prepared by the co-impregnation method for Si, Cu and Ni.



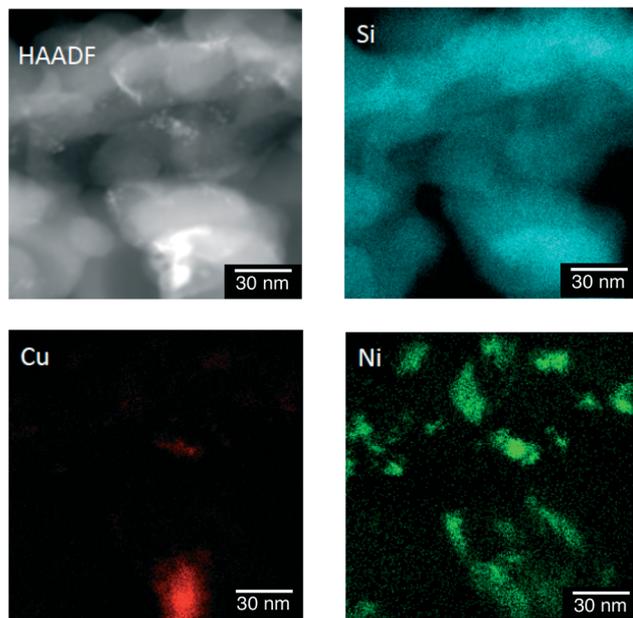


Fig. 7 HAADF-STEM and EDS elemental mapping of Ni-Cu/SiO₂ prepared by the sequential impregnation method (Ni loaded on Cu/SiO₂) for Si, Cu and Ni.

mapping for Cu (red) and Ni (green) with the HAADF-STEM image indicates that the brightest part of the HAADF-STEM image is the Cu-rich region, and the small particles that appeared in the upper middle are Ni rich or Ni only. These observations suggest that suitable selection of preparation methods is necessary to achieve close location of Ni and Cu on the surfaces of Ni-Cu/SiO₂.

2.4 Optimisation of Ni/Cu ratio, loading amount of Ni-Cu and structure of TiO₂ and SiO₂ supports

The catalytic activity of Ni-Cu/SiO₂ with different loading amounts of Ni-Cu [1 : 1 (w/w)] ranging from 2 to 5 wt% was examined for the photocatalytic H₂ evolution. The H₂ evolution rates determined from the slopes of time courses of H₂ evolution (Fig. 8a) at the reaction time from 5 to 30 min were

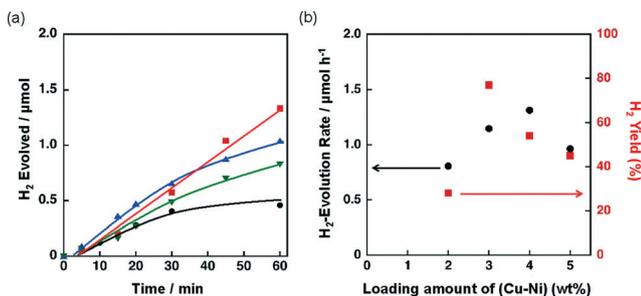


Fig. 8 (a) Time course of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and Ni-Cu/SiO₂ [Ni/Cu = 1/1 (w/w)] (100 mg L⁻¹; 2 wt%, black circle; 3 wt%, red square; 4 wt%, blue triangle; 5 wt%, inverted triangle) prepared by co-impregnation. (b) Effect of the loading amount of Cu and Ni on the initial (30 min) H₂ evolution rate and H₂ yield.

0.8, 1.2, 1.3 and 1.0 $\mu\text{mol h}^{-1}$ for Ni-Cu/SiO₂ with the loading amounts of Ni-Cu being 2, 3, 4 and 5 wt%, respectively. The total H₂ yield obtained for 3 wt% Ni-Cu/SiO₂ was 77%, which is higher than those for 2, 4 and 5 wt% Ni-Cu/SiO₂ (28%, 54% and 45%, respectively). Thus, the loading amount of Ni-Cu around 3–4 wt% is optimum to achieve high catalytic activity for Ni-Cu/SiO₂.

The effect of the ratio between Ni and Cu on the catalytic activity of 3 wt% Ni-Cu/SiO₂ was also examined. Fig. 9a shows the time courses of H₂ evolution in the photocatalytic H₂ evolution using Ni-Cu/SiO₂ catalysts with Ni contents, the Ni/(Ni + Cu) ratio, from 0% to 100%. H₂ evolution rates higher than 0.8 $\mu\text{mol h}^{-1}$ were observed for the catalysts with Ni contents from 25% to 67% as shown in Fig. 9b. The effect of Cu on the reducibility of NiO on SiO₂ has been discussed by temperature-programmed reaction with flowing H₂/Ar in the literature.^{35c-e} The reduction temperature of NiO on SiO₂ around 580 °C decreased to below 300 °C for Ni-Cu/SiO₂ under 10% flowing H₂/Ar.^{35c} The enhanced reducibility of NiO on Ni-Cu/SiO₂ catalysts resulted in high catalytic activity for ethanol steam reforming.^{35c} The promotional effect of Cu(O) on the reduction of NiO can also be expected for the present photocatalytic H₂ evolution system, although the reaction temperature was as low as room temperature.

Effects of the morphologies and the surface areas of SiO₂ supports on the catalysis of Ni-Cu/SiO₂ for H₂ evolution were also examined by employing two additional SiO₂ supports, which have a spherical morphology with the BET surface area similar to that of the SiO₂ support [unshaped, low surface area (unshaped LS)] used in the above experiments and an unshaped morphology with a higher BET surface area. The morphologies of SiO₂ supports were confirmed by TEM observations as shown in Fig. S7,[†] and the BET surface areas were determined to be 59 m² g⁻¹ and 420 m² g⁻¹ for the SiO₂ (spherical) and the SiO₂ [unshaped, high surface area (unshaped HS)], respectively. With these SiO₂ supports, 3 wt% Ni-Cu/SiO₂ catalysts [Ni/Cu = 1 : 1 (w/w)] were prepared by the co-impregnation method and used as the H₂ evolution

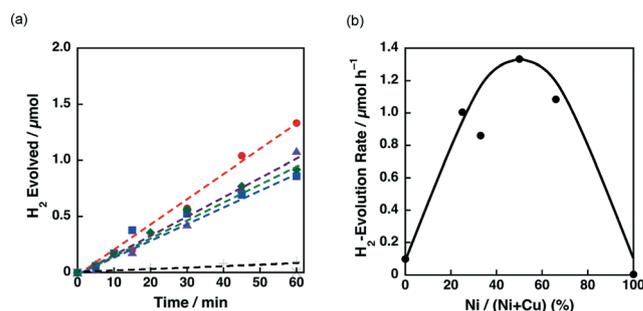


Fig. 9 (a) Time courses of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/SiO₂ (100 mg L⁻¹) with various Ni contents prepared by the co-impregnation method [Ni/(Ni + Cu) = 0% (plus), 25% (green diamond), 33% (blue square), 50% (red circle), 67% (purple triangle) and 100% (inverted triangle)]. (b) Plot of the initial H₂ evolution rate vs. Ni contents.



catalysts in the photocatalytic H₂ evolution system. The time courses of the H₂ evolution are shown in Fig. 10a. The H₂ evolution rates were 0.4 and 0.8 μmol h⁻¹ for Ni–Cu/SiO₂ catalysts with spherical and unshaped (high surface area) morphologies, respectively. The H₂ evolution rate for Ni–Cu/SiO₂ (spherical) being significantly lower than that for Ni–Cu/SiO₂ [unshaped LS (52 m² g⁻¹)] (1.3 μmol h⁻¹) indicates that the morphology of SiO₂ affects the catalysis of Ni–Cu/SiO₂. The lower catalytic activity obtained by employing SiO₂ (spherical) as a support has been reported for Ru/SiO₂ in the photocatalytic H₂ evolution.³⁰ The smooth surfaces of the SiO₂ (spherical) more readily promote the adhesive interaction among the SiO₂ particles through supporting metals than the rough surfaces of the SiO₂ (unshaped).³⁰ Thus, a part of the supporting metals acting as the adhesive among SiO₂ particles hardly work as the H₂ evolution catalyst. A similar mechanism is applicable to the present Ni–Cu/SiO₂ (spherical) catalysts. For the effects of surface areas, the catalytic activity of Ni–Cu/SiO₂ (unshaped LS) was higher than that of Ni–Cu/SiO₂ (unshaped HS). This result may suggest that the lower surface area of the SiO₂ is favourable to closely locate Ni and Cu to each other. Thus, both morphologies and surface areas of SiO₂ supports affect the catalysis of Ni–Cu/SiO₂.

The effect of the ratio between Ni and Cu was also investigated for 3 wt% Ni–Cu/SiO₂ (spherical) and 3 wt% Ni–Cu/SiO₂ (unshaped HS) in the photocatalytic H₂ evolution. The time courses of the H₂ evolution in the photocatalytic H₂ evolution are shown in Fig. S8.† Fig. 10b shows the relative H₂ evolution rates depending on the Ni/(Ni + Cu). High catalytic activity was achieved at the Ni contents between 30% and 67% as observed for Ni–Cu/SiO₂ (unshaped LS) shown in Fig. 9b.

The catalytic activity of Ni–Cu/TiO₂ for the H₂ evolution dependent on the Ni contents was also investigated in the photocatalytic H₂ evolution. Fig. 11a demonstrates the time courses of H₂ evolution in the photocatalytic reaction systems using Ni–Cu/TiO₂ with different Ni contents. H₂ evolution rates higher than 1.5 μmol h⁻¹ were obtained for the Ni–Cu/TiO₂ catalysts with 33–67% of Ni contents. The origin of the

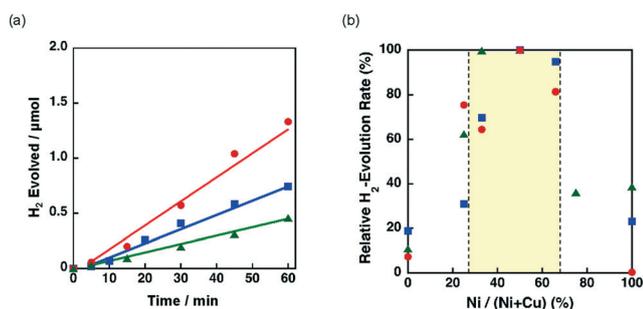


Fig. 10 (a) Time course of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni–Cu/SiO₂ (100 mg L^{-1}). (a) SiO₂ with a spherical morphology (green triangle) and unshaped LS (red circle) and unshaped HS (blue square). (b) Plot of the initial H₂ evolution rate vs. Ni contents.

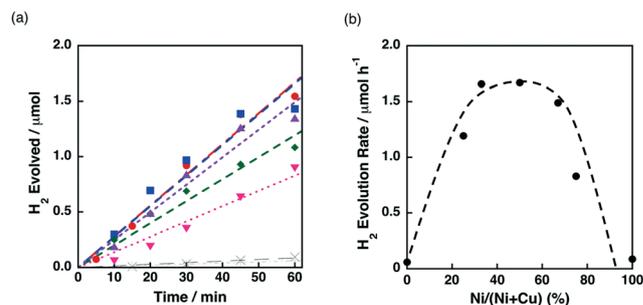


Fig. 11 (a) Time course of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni–Cu/TiO₂ (100 mg L^{-1}) with various Ni contents prepared by co-impregnation [Ni/(Ni + Cu) = 0% (plus), 25% (green diamond), 33% (blue square), 50% (red circle), 67% (purple triangle), 75% (pink inverted triangle) and 100% (cross)]. (b) Plot of the initial H₂ evolution rate vs. Ni contents.

synergistic effect of Ni and Cu on TiO₂ has been discussed by H₂-TPR measurements in the literature.^{41a} The reduction temperature of NiO on TiO₂ was lowered from *ca.* 500 °C to 300 °C in the presence of CuO by increasing the content of CuO.^{41a} Although the photocatalytic H₂ evolution was performed at room temperature, the readily reducible nature of NiO influenced by the addition of Cu would be beneficial to form metallic Ni species on the TiO₂ support.

Effects of crystal structures and the BET surface areas of TiO₂ supports were examined by using a series of 3 wt% Ni–Cu/TiO₂ catalysts in the photocatalytic H₂ evolution. The crystal structures confirmed by XRD (Fig. S9†) and BET surface areas of the TiO₂ supports were rutile with a high surface area (rutile HS, 250 m² g⁻¹), rutile with a low surface area (rutile LS, 0.3 m² g⁻¹) and anatase with a high surface area (anatase HS, 46 m² g⁻¹). The TiO₂ support used in the above-mentioned experiments has an anatase structure with a low surface area (anatase LS, 6.8 m² g⁻¹) (*vide supra*). With these TiO₂ supports, 3 wt% Ni–Cu/TiO₂ [Ni/Cu = 1 : 1 (w/w)] catalysts were prepared by the co-impregnation method. Fig. 12 shows the time courses of H₂ evolution in the photocatalytic H₂ evolution performed with these Ni–Cu/TiO₂ catalysts (rutile HS, rutile LS, and anatase HS) as the H₂ evolution catalysts. The H₂ evolution rates determined from the initial (60 min) slopes were 1.5, 1.3 and 1.3 μmol h⁻¹ for Ni–Cu/TiO₂ (rutile HS, rutile LS and anatase HS, respectively), which are comparable to that for Ni–Cu/TiO₂ (anatase LS) (1.7 μmol h⁻¹). Although the surface area of TiO₂ (rutile LS) is only *ca.* 1/1000 that of TiO₂ (rutile HS), the catalytic activity of Ni–Cu on these TiO₂ supports is comparable. These results suggest that neither the crystal structures nor the BET surface areas of the TiO₂ supports are insignificant factors to determine the catalytic activity of Ni–Cu/TiO₂.

3. Conclusions

The catalytic activity of Ni–Cu/TiO₂ and Ni–Cu/SiO₂ for H₂ evolution was greatly enhanced by the synergistic effects of



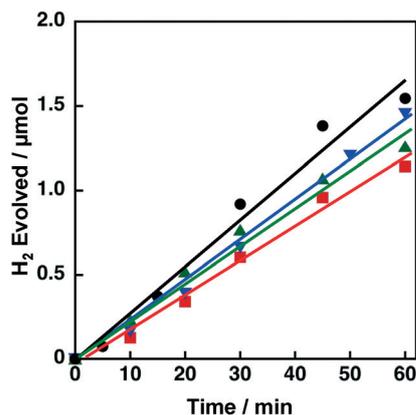


Fig. 12 Time course of H₂ evolution by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh⁺-NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu supported on TiO₂ (100 mg L⁻¹) with different crystal structures (anatase LS, black circle; rutile HS, blue inverted triangle; anatase HS, red square; rutile LS, green triangle).

Ni and Cu on the photocatalytic H₂ evolution system using 2-phenyl-4-(1-naphthyl)quinolinium ion and NADH as a photocatalyst and an electron donor, respectively. Such a synergistic effect between Ni and Cu was not observed for Ni-Fe and Ni-Co catalysts and for Ni-Cu/SiO₂-Al₂O₃ and Ni-Cu/CeO₂. TEM observation and EDS elemental mapping of Ni-Cu/SiO₂ prepared by the co-impregnation and the sequential impregnation methods suggest that the close location of Ni and Cu is important to achieve the high catalytic activity. The synergistic effect between Ni and Cu was observed in the wide range of Ni contents, Ni/(Ni + Cu), from 30% to 70%. This study has demonstrated that suitable choices of additives, supports, and catalyst preparation methods are all important to achieve highly active H₂ evolution catalysts composed of base metals with synergistic effects.

4. Experimental section

4.1 Materials

All chemicals were obtained from chemical companies and used without further purification. SiO₂ (unshaped, low surface area), TiO₂ (anatase, low surface area) and TiO₂ (anatase, high surface area) were purchased from Sigma-Aldrich. SiO₂ (unshaped, high surface area) was obtained from Merck. Iron nitrate, copper nitrate, nickel nitrate, 2-propanol, hydrochloric acid (37%), sodium aluminate and titanium(IV) chloride were obtained from Wako Pure Chemical Industries. Aqueous ammonia (28%) and β -dihydronicotinamide adenine dinucleotide disodium salt (reduced form) (NADH) were obtained from Tokyo Chemical Industry. Tetraethyl orthosilicate (TEOS) was delivered by Shin-Etsu Chemical. Acetonitrile was obtained from Nacalai Tesque. CeO₂ was provided by Daiichi Kigenso Kagaku Kogyo Co., Ltd. 2-Phenyl-4-(1-naphthyl)quinolinium perchlorate (QuPh⁺-NA),⁴² SiO₂-Al₂O₃,⁴⁶ spherical SiO₂,⁴⁷ and TiO₂ (rutile, high surface area)⁴⁸ were

prepared by literature methods. Purified water was provided by using a Millipore DIRECT-Q UV3 water purification system (18.2 M Ω cm).

4.2 Preparation of Ni-Cu supported on metal oxides by a co-impregnation method

A typical procedure for the preparation of metal oxides supporting Ni and Cu by a co-impregnation method is as follows: metal oxide (350 mg) was soaked in an ethanol solution (30 mL) containing Ni(NO₃)₂·6H₂O (26.8 mg, 92.2 mmol) and Cu(NO₃)₂·3H₂O (20.6 mg, 85.3 mmol) and sonicated for 30 min. The obtained catalyst precursor was dried at 60 °C in an oven and calcined at 350 °C (ramp rate: 5 °C min⁻¹) for 4 h in air. The obtained powder was soaked in an ethanol solution containing NaBH₄ to reduce oxides of Cu and Ni before catalysis evaluation.

4.3 Preparation of Ni-Cu supported on TiO₂ and SiO₂ by a sequential impregnation method

A typical procedure for the preparation of TiO₂ and SiO₂ catalysts supporting Cu and Ni by a sequential impregnation method is as follows: TiO₂ or SiO₂ (350 mg) was immersed in an ethanol solution (30 mL) containing Cu(NO₃)₂·3H₂O (20.6 mg, 85.3 mmol) and sonicated for 30 min. The obtained catalyst precursor was dried at 60 °C in an oven and calcined at 350 °C (ramp rate: 5 °C min⁻¹) for 4 h in air. Then, the calcined sample was immersed in an ethanol solution (30 mL) containing Ni(NO₃)₂·6H₂O (26.8 mg, 92.2 mmol). The obtained slurry was dried and calcined. The obtained powder was soaked in an ethanol solution containing NaBH₄ to reduce oxides of Cu and Ni before catalysis evaluation.

4.4 Preparation of Ni-Co and Ni-Fe supported on TiO₂ and SiO₂ by a co-impregnation method

These catalysts were prepared by a co-impregnation method as follows: TiO₂ or SiO₂ (350 mg) was soaked in an ethanol solution (30 mL) containing Ni(NO₃)₂·6H₂O (26.8 mg, 92.2 mmol) and Co(NO₃)₂·6H₂O (26.8 mg, 92.1 mmol) or Fe(NO₃)₃·9H₂O (37.2 mg, 92.1 mmol) and sonicated for 30 min. The obtained catalyst precursor was dried at 60 °C in an oven and calcined at 350 °C (ramp rate: 5 °C min⁻¹) for 4 h in air. The obtained powder was soaked in an ethanol solution containing NaBH₄ to reduce oxides of Cu and Ni before catalysis evaluation.

4.5 Preparation of SiO₂-Al₂O₃

SiO₂ was suspended in an aqueous solution (50 mL) containing sodium aluminate (1.3 g, 16 mmol) and stirred for 20 h at room temperature. The precipitate was collected by filtration and dried at 120 °C. The dried sample was calcined at 550 °C (ramp rate: 5 °C min⁻¹) for 6 h in air.



4.6 Preparation of spherical silica

TEOS (18 mL, 80 mmol) was dissolved in a mixture solution of water (31 mL), ethanol (300 mL) and 28% ammonia solution (5.4 mL) and stirred for 4 h at room temperature. After the reaction, the obtained white precipitate was collected by centrifugation (9000 rpm, 10 min) and washed three times with water. The obtained powder was dried at 70 °C in an oven and calcined at 350 °C (ramp rate: 5 °C min⁻¹) for 4 h in air to remove residual ammonia.

4.7 Preparation of TiO₂ (rutile, high surface area)⁴⁸

Titanium(IV) chloride (5.7 g, 30 mmol) was dissolved in a mixture solution of water (100 mL), 2-propanol (200 mL) and hydrochloric acid (10 mL) and refluxed for 20 h at 90 °C. After the solution was cooled to room temperature, the suspension was basified to pH 9 with 28% ammonia solution. The white precipitate was collected by centrifugation (9000 rpm, 10 min) and washed three times with water.

4.8 Preparation of TiO₂ (rutile, low surface area)

TiO₂ (rutile, high surface area) was calcined at 1000 °C (ramp rate: 10 °C min⁻¹) for 3 h in air.

4.9 Transmission electron microscopy (TEM)

The sizes and shapes of SiO₂ supports were determined from bright-field images using 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 dispersion of catalysts onto the support and allowing the solvent to evaporate and then scooping up with an amorphous carbon supporting film on a Cu grid. High-angle annular dark-field scanning TEM (HAADF-STEM) images and the energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Ni-Cu/SiO₂ were obtained by using an FEI Titan G2 60-300 with an accelerating voltage of 300 kV. The observed samples were directly put on Mo meshes.

4.10 Catalyst characterisation by powder X-ray diffraction, diffused reflectance UV-vis spectroscopy and dynamic laser scattering

X-ray diffraction patterns were recorded with a Rigaku MiniFlex 600. Incident X-ray radiation was produced by using a Cu X-ray tube operating at 40 kV and 15 mA with a Cu K α radiation of 1.54 Å. The scanning rate was 2° min⁻¹ from 5° to 80° in 2 θ . The diffuse reflectance UV-vis spectra were recorded with a Jasco V-670 spectrophotometer equipped with an integrating sphere module (SIN-768). Reflectance obtained for each sample was converted to $f(R_\infty)$ values according to the Kubelka-Munk theory, $f(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the reflectance of the sample layer. BaSO₄ was used for background spectra measurements. Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., USA).

4.11 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 an adsorbed amount of N₂ was calculated from the change in 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.

4.12 Photocatalytic H₂ evolution

A mixed solution (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (0.88 mM), NADH (1.0 mM) and an H₂ evolution catalyst was flushed with N₂ gas. The solution was then irradiated 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 of stirring in the dark, the gas in the headspace was analysed by Shimadzu GC-14B gas chromatography (detector: TCD, column temperature: 50 °C, column: active carbon with the particle size of 60–80 mesh, carrier gas: N₂ gas) to determine the amount of evolved H₂.

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